# Smart amphiphiles: hydro/organogelators for *in situ* reduction of gold†

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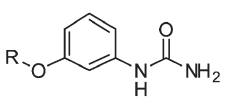
**New urea containing gels have been used to prepare and stabilise gold nanoparticles by *in situ* reduction.**

Chemists are intrigued by the development of various synthetic protocols for the synthesis of nanoscale functional materials.[1] Gels represent one example of this functional architecture, whereby the self-assembly of low molecular weight amphiphiles into nanoscale fibers that entangle to form 3D fibrous networks results in the macromolecular organization of liquids into solid or semi-solid gels.[2,3] Supramolecular gels are known to form various exotic nanoaggregates such as fibers, thin sheets, helical and lamellar structures.[4] These gels are finding increasing use in templated materials,[5] drug delivery, cosmetics, separations, and biomimetics.[4,6] However, there are only two available reports describing nanoparticle preparation in gels.[7] Kimura *et al.* reported the entrapment of gold nanoparticles (GNPs) in gels using a thiol-terminated gelator. They made a physical mixture of the hot gel solution with preformed alkylthiol stabilised GNPs and further gelation produced GNPs assembly on a fibrous gel network.[7a] More recently, Love *et al.* reported GNPs synthesis in organogel,[7b] by diffusing tetraoctylammonium bromide stabilised $HAuCl_4$ toluene solution into preformed toluene gel and subsequent UV irradiation. However, to the best of our knowledge there are no reports on the *in situ* preparation of GNPs using low-molecular-weight hydrogelators. While one would expect gels to form various types of nanoaggregates, if the gelator itself can act as reducing and capping agent to synthesize GNPs, what would be the distribution and stability of GNPs in the gel? Are they distributed all over the gel? Or are they aligned in a particular orientation along with the gel microstructures? This is especially interesting in building aligned arrays of GNPs for possible optical device applications.




**1**: R = *n*-$C_6H_{13}$
**2**: R = *n*-$C_{10}H_{21}$
**3**: R = *n*-$C_{14}H_{29}$

To address these questions, we synthesized various mono-substituted urea derivatives, **1–3** (ESI†). These amphiphiles were found to be efficient gelators for water and various organic solvents and carry a free terminal amine group which possibly reduces the gold to form GNPs.[8] Although various research groups have developed urea and thiourea based hydro/organo gelators[4,9] they have never been explored for the *in situ* preparation of GNPs.

Urea derivatives **1** and **2** form gels in water and in various organic solvents such as cyclohexane, benzene, toluene and $CCl_4$. Gelator **3** also forms gels in the above mentioned solvents and in addition it forms gels in polar solvents like methanol, ethanol, acetone and dioxane (a small 1–3 v/v% of EtOH as co-solvent required for water). **3** forms gel in water when present in amounts as low as 0.1 wt% and in cyclohexane 0.2 wt% (wt/vol). Minimum gelation concentrations (MGC) and gel melting temperatures ($T_{gel}$) for these gelators in various solvents are listed in Table 1 (ESI).

Gelation tests were carried out in the following way: the required amount of gelator was added to the solvent and the mixture heated to 50–70 °C to form a clear solution; upon cooling to room temperature gels were formed. These gels are thermoreversible and stable for a few months. Gel melting ($T_{gel}$) experiments were carried out using a typical "inversion tube" method[10] and differential scanning calorimetry (DSC). All these gels showed good thermal stabilities; DSC determined $T_{gel}$ of hydrogels from **1**, **2** and **3** were 70, 84 and 92 °C respectively.

Hydro/organo gels of urea derivatives were characterised by using scanning (SEM) and transmission (TEM) electron microscopy. Scanning electron micrographs of xerogels prepared from gels of 0.1 wt% of **2** in water are shown in Fig. 1a. These gelators formed aggregated planar sheets indicating some local crystallinity that could be due to the extensive hydrogen bonding network of the urea group.

Amines, such as oleylamine, are known to reduce Au(III) to Au(0) to form GNPs.[8] We wanted to explore the possibility of using urea amphiphiles as reducing agents for $HAuCl_4$, followed by capping. Due to the presence of a free terminal $NH_2$ group **1–3** could be used for capping the GNPs. To test this, we added 1 mg of **2** to the $HAuCl_4$ solution and heated the mixture to around 40–50 °C to produce a homogeneous solution; it could be seen that the yellow coloured solution initially became colourless

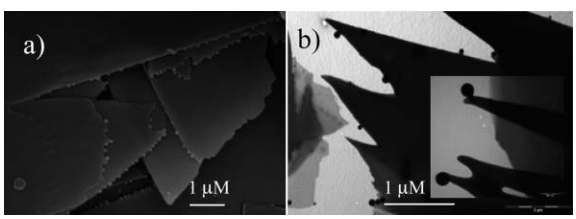



**Fig. 1** SEM image of xerogels prepared from gels of a) **2** in water and sheets with GNPs. TEM image of b) hydrogel of **1** with GNPs (inset magnified range).

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† Electronic supplementary information (ESI) available: Synthetic scheme and procedure, gelation properties, additional EM and XRD data. See DOI: 10.1039/b518289a

 

[Au(III) to Au(I)] then turned to a pink hue, indicating the reduced form of gold. After allowing the solution to come to room temperature GNPs embedded pink coloured gel formed.

We characterised GNPs embedded gels by using SEM and TEM (Fig. 1a and b). Formation of gels in presence of GNPs did not change the basic morphology of the gel. More interestingly, the edges of all gel platelets were decorated with GNPs as we can see in Fig. 1a. More careful analysis by TEM showed the presence of well-dispersed GNPs and in a few instances they formed occasional large clusters and were segregated from planar sheets, which were arranged on the edges of the gel sheets (Fig. 1b, for schematic representation see ESI). We also prepared GNPs by using **1** in acetone solution (**1** does not form gel in acetone); the resulting **1**-protected GNPs were soluble and stable for a few months. TEM images show that the resulting spherical GNPs were uniform in size (11–15 nm) and mostly dense regions were observed (ESI). However, **3** reduced/capped GNPs in acetone gel were well separated and uniformly distributed with a spherical shape (ESI). GNPs embedded gels were dried and dissolved in acetone and subjected to UV-vis spectroscopy. As shown in Fig. 2c, this sample showed a characteristic plasmon resonance band at 553 nm indicating the existence of gold particles in nanoscale dimensions. We hypothesized that the terminal amine group of the urea amphiphile is acting as a reducing agent, subsequently binding to Au(0) to stabilize them. To shed light on this hypothesis, we synthesized 3-decyloxyacetanilide, which resembles the structure of **2** except that methyl replaces the terminal amine group, and this lack of a terminal amine group should prevent the gold reduction process. We tested the gelation of the acetanilide derivative, which still forms gels in water in presence of 20% MeOH as co-solvent, but failed to reduce the $HAuCl_4$ under similar conditions to produce the GNPs. These results unambiguously prove that the terminal amine group of the urea is essential in the gold reduction process. However, presence of GNPs in gels did not change bulk properties (MGC and $T_{gel}$) of gels significantly.

The hydro- and organogels obtained from **1–3** displayed well-resolved X-ray diffraction patterns that were characteristic of the long-range ordering of the molecules (ESI). These gels showed periodical reflection peaks, which indicates that these gelators assemble into a lamellar organization. GNPs doped hydrogels showed a characteristic (111) peak in XRD confirming the presence of GNPs in the gels (ESI).

To gain more insight into the driving forces behind the self-assembly of urea based amphiphiles we carried out temperature variable $^1$H-NMR experiments. The gel forming ability of **3** in $CHCl_3$ gave us the opportunity to conduct NMR experiments in $CDCl_3$; typical $^1$H-NMR spectra are shown in Fig. 2b. Intriguingly, at 60 °C (above $T_{gel}$) the amide NH peak at 6.25 ppm shifted to downfield significantly while becoming sharper compared to the peak at 25 °C, which clearly suggests amide NH proton participation in hydrogen bonding. Similar behaviour was observed in the case of terminal $NH_2$ protons at 4.6 ppm (Fig. 2b inset). In addition to that, broadening of aromatic proton peaks in the gel phase (25 °C) also suggests the existence of π–π stacking. Information obtained from the NMR experiments tells of nanoscopic aggregation, and thus we believe the similar mode of the aggregation would be transformed into the macroscopic level. Previously similar NMR results were observed with different gel systems.[3] Further, FT-IR experiments also suggested that urea groups were involved in hydrogen bonding (see ESI). Taking together the NMR, FT-IR and XRD results, we propose a possible model for the self-assembly of these amphiphiles which is shown in Fig. 2d.

In conclusion, we have developed urea-based aryl derivatives as gelators, which showed excellent gelation ability in a broad range of solvents from water to cyclohexane. These gelators were successfully used for the first time in the synthesis of GNPs as reducing and capping agents, showing the essential nature of the free amino group for the reduction and further capping process. Importantly, after reduction of gold they retain their gelation properties intact, hence entrapping the GNPs in the supramolecular assemblies. Such materials should provide opportunities for the development of nanostructured-advanced materials from the conjugates of gels and metal nanoparticles, which may uncover applications in the promising field of supramolecular devices.

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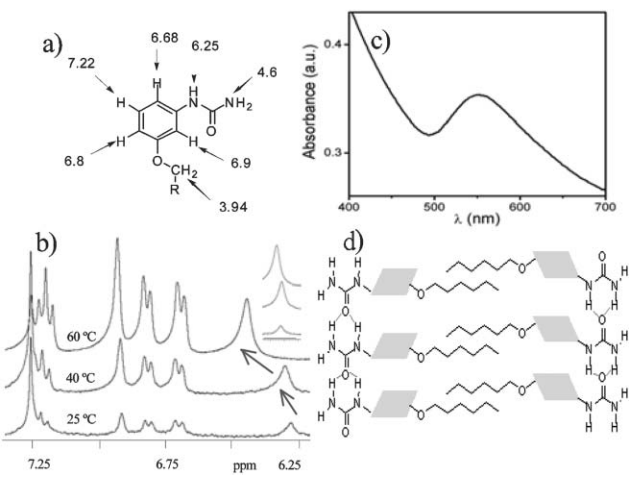


**Fig. 2** a) Chemical shift assignment of **3**. b) Temperature variable $^1$H-NMR for hydrogel of **3**, inset 4.6 ppm region. c) UV-vis spectra of GNPs embedded hydrogel of **3**. d) Possible molecular arrangement of hydrogels; alkyl chain does not represent exact chain length.

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