Solubility switch of gold nanoparticles through hydrogen bond association†

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Gold nanoparticles (AuNPs) coated with hexafluoroisopropanol moieties were prepared, and their surface was changed through simple hydrogen bond association with various amines, which allow orientation of the solubility of these AuNPs in determined organic solvents.

During recent years, a great attention has been paid to the functionalisation of gold nanoparticles (AuNPs).[1] The applications they are designed for often need to answer to a water-solubility request and suppose thus polar interactions with aqueous media.[2] For this purpose, nanoparticles coating with hydrophilic ligand molecules has been shown to be a very effective approach.[2] Alternatively, it is possible to orientate the solubility of AuNPs towards organic media through polarity modulations at the surface of the nanoparticles by using an appropriate ligand.[3] Consequently, such materials could become compatible with a large variety of polymeric matrices and find application in material science.[4] However, getting a kind of nanoparticles that would be soluble in a wide range of organic solvents with very different polarities (*e.g.* from alcohols to alkanes) invalidates a simple coating approach, since a different ligand would be required for each solvent.[5] *In theory, a powerful alternative would be to synthesize a single AuNPs type with a polarity that could be easily tuned through simple transformations*. In order to get such "ubiquitous" AuNPs, grafting gold with a very particular and original organic compound is required. In the last years, hexafluoroisopropanol (HFIP) has been in the focus of many investigations[6] because of its unique and remarkable features: very strong hydrogen bond donor ability, high acidity (pK_a in water = 9.3) and polarity.[7] Among the unique characteristics of HFIP, the hydrogen bond donation is particularly important, as exemplified by the facile formation and isolation of a crystalline HFIP–piperidine complex that has been recently characterised by X-ray.[8] The crystallinity of this complex as well as its high stability demonstrate the strength of the hydrogen bonds. The transfer of these remarkable properties of HFIP to nanomaterials would be of prime interest. In this context, we report herein the synthesis of gold nanoparticles functionalized with HFIP derivatives (HFIP-AuNPs), the investigation of the associations through hydrogen bonds between this new hybrid material and amines, and their effect on the solubility of the HFIP-AuNPs.

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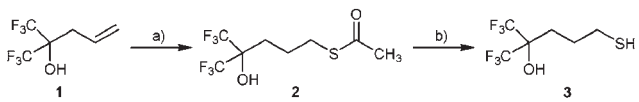
A straightforward and reliable method for functionalising AuNPs involves reduction of gold(III) compounds, under either bi- or monophasic conditions, in the presence of the ligand, usually a thiol or a disulfide.[9,10] In order to get a ligand bearing both a thiol and an hexafluoroisopropanol moities, we used allylHFIP **1** as starting material. The radical addition of thioacetic acid onto allylHFIP **1**, followed by a reduction of the obtained thioester **2** with $LiAlH_4$ in THF afforded the ligand **3** in almost quantitative yield (Scheme 1).‡

Due to the acidity of the HFIP moiety of **3** which might perturbate the coating of AuNPs, an adapted process should be required. In 1995, Brust and Schiffrin reported a single-phase method to prepare AuNPs functionalized with a mercaptophenol moiety.[10] According to the similar acidities of phenol and HFIP, this method seemed to fit perfectly. Thus, the simultaneous reduction of tetrachloroaurate ($AuCl_3$·HCl), with aqueous sodium borohydride, and anchoring of organic thiol molecules were performed in methanol at room temperature. The reaction was conducted in the presence of a catalytic amount of acetic acid to prevent the deprotonation of the alcohol.[10] By this procedure, HFIP-derived gold nanoparticles (HFIP-AuNPs) were afforded as a sticky brown solid with an average particle diameter of 2.8 ± 1.4 nm, as shown in Fig. 1.

The HFIP-AuNPs are soluble in polar organic solvents like methanol or ethyl acetate (AcOEt), insoluble in apolar organic media and in water. They are stable at room temperature for several months.

According to the properties of HFIP, we reasoned that HFIP-AuNPs should bind to amines, leading thus to an overcoating of the nanoparticles with surface properties directly depending on the amine type. Briefly, the experiments were performed by adding dropwise an AcOEt solution of HFIP-AuNPs to a solution of a polar diamine in AcOEt [piperazine or DABCO (1,4-diazabicyclo[2.2.2]octane)], which provoked the formation of a precipitate. Removal of the solvent, followed by an elimination of the excess of amine with water afforded the expected amine/HFIP-AuNPs complex: the elemental analysis revealed that 0.4 molecule of diamine is present for one alcohol moiety. The formation of this second layer around the nanoparticles dramatically modifies their properties: they appear as a stable dark-brown powder, and they have a very poor solubility in AcOEt, while the original HFIP-AuNPs was a



1 2 3

Scheme 1 Synthesis of thiol **3**: *Reagents and conditions*: (a) thioacetic acid, AIBN, dichloroethane, reflux, 6 h, 98%; (b) $LiAlH_4$, THF, room temperature, 1 h, 99%.

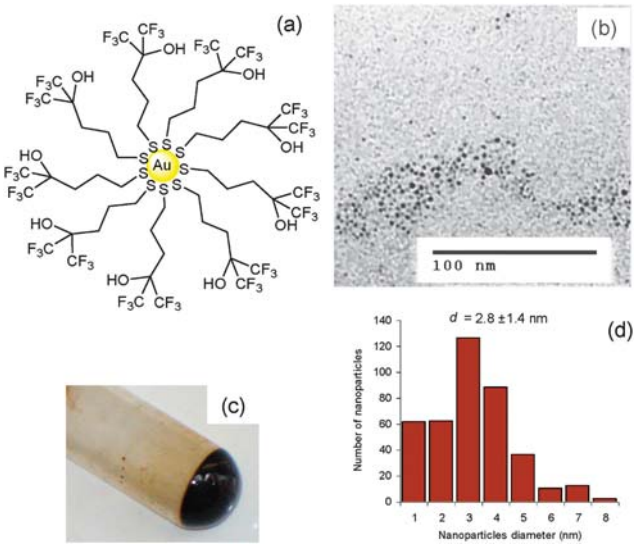


Fig. 1 HFIP-AuNPs: (a) Schematic depiction; (b) TEM micrograph; (c) aspect; (d) size histogram.

sticky solid completely soluble in AcOEt (Fig. 2). However, the nanoparticles size remains in the same range ($d \cong 2.8$ nm).

Since the formation of an outer layer around the HFIP-AuNPs by hydrogen bonding with amines strongly modifies the surface properties, this effect could probably be tuned by using different type of amines. In this line, by using mono-amines with hydrophobic chains as complexation partners it is reasonable to expect a "solubility switch" towards apolar media. Indeed, this protocol performed with tributylamine, afforded a complex with $\sim$0.3 molecules of amine per alcohol function and made the resulting Bu_3N/HFIP-AuNPs soluble in dichloromethane. Finally, the most striking effect was obtained with the apolar tridodecylamine n-$(C_{12}H_{25})_3N$. In this case, the surface polarity change was so important that a complete solubility switch was observed: the nanoparticles obtained became completely soluble in alkanes such as petroleum ether or pentane (Fig. 3).

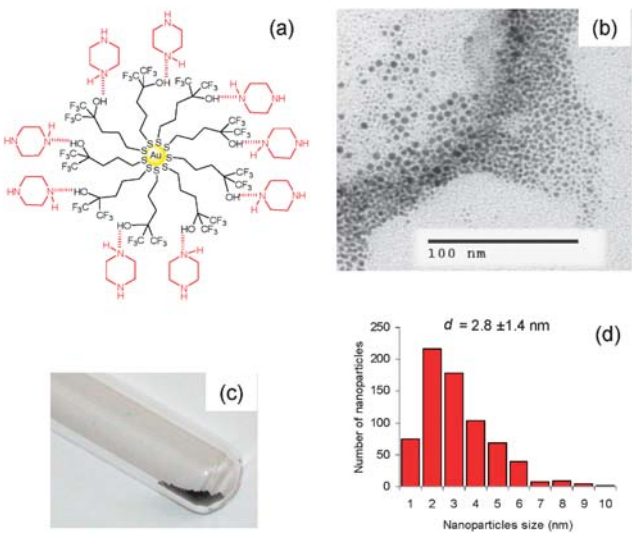


Fig. 2 Piperazine/HFIP-AuNPs complex: (a) schematic depiction; (b) TEM micrograph; (c) aspect; (d) size histogram.

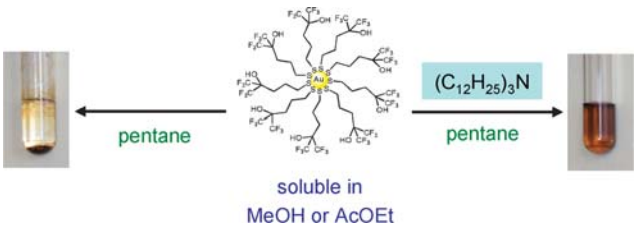


Fig. 3 Solubility switch of HFIP-AuNPs by hydrogen bonding with an apolar amine

In this latter case, it is worth noting that the diameter of the particles ($d = 4.0 \pm 2.3$ nm) significantly increased by more than 1 nm with respect to the original HFIP-AuNPs and former complexes.

In conclusion, we have synthesized "ubiquitous" gold nanoparticles coated with an HFIP derivative (HFIP-AuNPs) that can be selectively soluble in an organic solvent ranging from methanol to pentane. This polarity tuning is obtained by amine overcoating through hydrogen bonds. These results are very promising for the compatibility of gold nanoparticles with a wide variety of matrices.

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