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Review

Gold nanoparticles protected by fluorinated ligands: Syntheses, properties and applications

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ABSTRACT

The development of fluorinated gold nanoparticles is presently arising and increasing attention across several fields of nanotechnology. The synthetic approaches evolved over time from the use of almost perfluorinated alkanethiols and perfluorinated arylthiols to amphiphilic fluorinated thiols capable of ensuring solubility in conventional organic solvents and water. The interest in these systems stems from the unique properties of both nanosized and fluorous compounds. In perspective, the development of our understanding of the fluorophilic interactions at the nanoscale will allow to devise novel strategies for self-assembly, molecular recognition and new materials for biomedical applications. In this paper we present, through selected examples, the potential of fluorous ligands in the synthesis of gold nanoparticles and the relevance of mastering the properties of these systems in the development of new materials.

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Contents

1. Introduction	000
2. "Perfluorinated" gold nanoparticles	000
3. Fluorous gold nanoparticles with improved solubility properties	000
4. Fluorous monolayers in 3D: Host–guest chemistry, monolayer structure, assembly properties and applications	000
4.1. Host–guest chemistry	000
4.2. Monolayer structure	000
4.3. Assembly properties	000
4.4. Assembly by halogen bonds	000
4.5. Applications of fluorous nanoparticles	000
5. Toxicity of fluorous gold nanoparticles	000
6. Perspectives	000
Acknowledgements	000
References	000

1. Introduction

Gold nanoparticles with sizes in the range of 1–100 nm protected by a monolayer of chemisorbed thiolates are the

subjects of intense research because their size-dependent properties enable a rich variety of novel materials to be obtained. This interest spans different fields of nanotechnology and material sciences, from self-assembly of higher order structures [1], catalysts [2] and sensors development, to applications in the medical field [3] such as delivery of therapeutics [4–6] and diagnostics [7,8]. This popularity is certainly bound to their ease of preparation and functionalization; by the possibility of manipulating these systems like common organic compounds and, moreover, by the possibility of using conventional analytical

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techniques for their purification and characterization. These properties stem from the stability of the monolayer that protects, or passivate, the particles, which also dictates much of the chemical behavior of these systems in their interactions with other species. From this viewpoint, gold may be considered a convenient choice, making gold nanoparticles an easily accessible model to study the monolayer chemistry of nanosized objects. Historically, the first reliable synthesis of gold nanoparticles protected by an organic monolayer of thiolate ligands was developed by Brust and Schiffrin [9]. They reported the formation of monolayer protected gold nanoparticles by reduction of HAuCl_4 with sodium borohydride in the presence of excess dodecanethiol and tetraoctyl ammonium bromide as phase transfer agent. The homoligand systems obtained were stable in solution and in the solid state and freely soluble in common apolar solvents. The second major step in gold nanoparticles chemistry come after the discovery of the place exchange reaction [10] by Murray and coworkers that enabled the introduction of a rich variety of functional thiols in the monolayer of preformed nanoparticles. Virtually any functional group can be introduced in the monolayer of gold nanoparticles by this method. This is particularly useful when functional thiols cannot be used in the Brust–Schiffrin procedure; either because of limited stability under reducing conditions or because synthetic limitations hamper the use of the excess thiol needed in the direct synthesis. In the mixed monolayer nanoparticles obtained the ligands could be arranged in a random distribution, essentially maximizing the entropy of mixing, or, on the contrary, may form segregated domains. This was actually found to be true under well-defined geometric and thermodynamic constraints [11,12]. The formation of monolayer domains made of different thiols is a source of chemical anisotropy on an otherwise very symmetric surface. This is the starting point to devise nanoparticles based building blocks to assemble (or to induce the self-assembly of) higher order structures in a predictable and programmable manner. In this respect, extreme phase segregation can be achieved by exploiting the tendency of fluorocarbon chains (F-Chains) and hydrocarbon chains (H-Chains) to self-sort. Homoligand or heteroligand fluorinated nanoparticles, however, may display markedly low solubility in common solvents, posing severe limitations to their purification, characterization and applications. To overcome this problem, the fluorinated moieties need to be shielded from the bulk solvent by using suitably solubilizing units with the penalty of an increased synthetic effort. These systems are ideal models to analyze the scope of using fluorinated nanoparticles in solvent systems such as water or biological media that would have been otherwise inaccessible.

2. “Perfluorinated” gold nanoparticles

Early attempts of synthesis of nanoparticles by using heavily fluorinated alkanethiols, typically the commercially available 1*H*,1*H*,2*H*,2*H*-perfluoro alkanethiols and pentafluorobenzenethiol led to materials of very low solubility that proved to be difficult to purify and characterize. Among these early attempts, the first preparation of perfluorinated silver nanoparticles was reported by

Korgel [13] in 2000 by using **1** in a modified Brust–Schiffrin procedure. Later, the synthesis of gold (and silver) nanoparticles was reported by Yonezawa and Kimizuka [14,15] in 2001 by using a single phase (ethanol) method in the presence of **1** or **2**, Fig. 1. The material obtained precipitated off the solution because of the poor solvating properties of ethanol for these systems. The nanoparticles' core had a mean diameter of 2.4–2.6 nm and these systems were essentially insoluble in several organic solvents while they were readily soluble in fluorocarbons including hexafluorobenzene, perfluorobutylalkyl ethers and in HCFC225 (mixture of $\text{CF}_3\text{CF}_2\text{CCl}_2\text{H}$ and $\text{CF}_2\text{ClCF}_2\text{CClFH}$).

The characterization of the nanoparticles by TEM analyses revealed a narrow size distribution with a strong tendency of forming 2D superlattices onto the TEM support. The gap between adjacent gold cores in the 2D-lattice was smaller than twice the length of the thiolate ligand, with strong indication that self-assembly was led by interdigitation of F-chains of neighboring particles. Other early examples of perfluorinated nanoparticles of smaller size, comprising 44–75 gold atoms in their core were reported by Murray and coworkers [16]. These nanoparticles were prepared by two different synthetic methods: (i) the reaction of **1** with tetrachloroauric acid in a typical Brust–Schiffrin procedure and (ii) by reaction of the molecularly precise gold cluster $\text{Au}_{55}(\text{PPh}_3)\text{Cl}_6$ with pentafluorobenzenethiol **3**. As observed by Yonezawa, the materials obtained displayed solubility only in fluorocarbons. In the preparation of nanoparticles according to the Brust–Schiffrin method, that employs tetraoctylammonium bromide as phase transfer agent, the authors observed a significant reduction of the solubility by increasing the number of washing cycles needed to remove the excess phase transfer agent. This was a clear indication that the fluorinated nanoparticles were able to trap this species, a behavior never reported for hydrogenated nanoparticles. However, it was not clear whether the ammonium ion was adsorbed in the monolayer or entrapped in the nanoparticles precipitate. Such a distinction is crucial because in the former case it would have indicated the tendency of fluorinated nanoparticles to take place in molecular recognition events, in spite of the tendency of fluorocarbons and hydrocarbons to form separate phases. In the synthesis reported by Murray the nanoparticles' size was much smaller than that obtained by Yonezawa, but was still polydispersed as could be inferred from UV–vis analysis. In the preparation that employed the Au_{55} template, the structural integrity of the cluster was not retained and the reaction occurred with the formation of larger particles, including Au_{75} clusters, identified by voltammetric techniques because of its typical band gap. This behavior was not directly due to the fluorinated thiols because it was also observed with hydrogenated alkanethiols [17]. An application of these perfluorinated nanoparticles was reported by Whitten [18]: thin films of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiolate protected gold nanoparticles were proved to uptake solvents in the vapour phase with a selectivity order: Hexafluorobenzene > methanol > hexane > chloroform > toluene = water. The electrical resistance of the nanoparticles' film decreased with vapor exposure, while the opposite behavior was observed with mercaptohexadecanic acid protected nanoparticles used as reference. The authors attributed this behavior to the porous

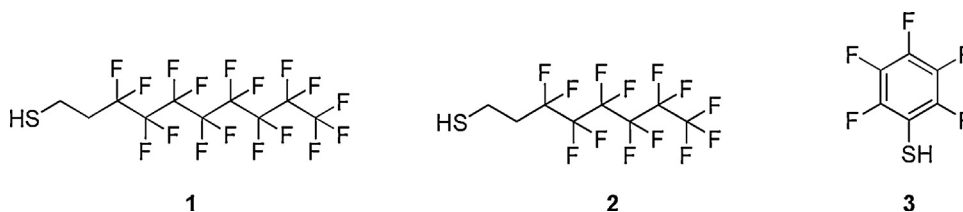


Fig. 1. Structures of the (quasi) perfluorinated alkanethiols and aryl thiols used in the early synthesis of fluorinated gold nanoparticles.

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