

## Selective Iron (II) colorimetric sensor based on hydroxamic acid-functionalized gold nanoparticles

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**Abstract:** We have synthesized thiol functionalized gold nanoparticles through ligand exchange reactions. Metal-mediated nanoparticle assembly was studied using mixed monolayer protected gold clusters. Transmission electron microscopy (TEM) was used to determine the nano scale structure of these aggregates. <sup>1</sup>H NMR and FT-IR spectroscopy were used to characterize the structure of these nanoparticles. The primary MPNs(monolayer protected nanoparticles) stabilized with alkanethiol were modified to increase the capability of nanoparticles in reaction with metal ligands to form metal complexes. These modified gold nanoparticles are more able to bond with metals such as Iron (II) as the ligand in formation of chemical sensors. The formation of metal complexes was monitored by UV-vis spectroscopy.

**Keywords:** Gold nanoparticle; SAM; MPN; Alkan thiol.

### Introduction

Nanoparticles are micro structures with unique properties which can be used in several applications. The assembly of nanoparticles into macro structures provides nanocomposites featuring useful chemical, electronical, and physical properties [1, 2].

At these sizes, nano systems can exhibit interesting and useful physical behaviors. Chemistry has played a key role in the development of nanoscience. Making and breaking bonds between atoms or groups of atoms is a fundamental component of chemistry. The development of new synthetic methods has made it possible to produce uniform nanostructures with new shapes [3]. Self-assembled mono layers (SAMs) are molecular aggregates that are spontaneously formed by the adsorption of amphifunctional molecules on a solid surface. There are several types in self-assembly methods that give organic mono layers. These include organosilicon on hydroxylated surfaces (SiO<sub>2</sub> on Si, Al<sub>2</sub>O<sub>3</sub> on Al, glass, etc.), alkanethiolates on gold [4], silver, and copper, alcohols and amines on platinum, and carboxylic acids on aluminum oxide, silver oxide, and glass. From the energetic point of view, a self-assembling surfactant molecule consists of three parts [5].

There are generally two factors that drive the formation of a mono layer [6, 7], a strong interaction between the head-group and the surface. SAMs provide a convenient, flexible, and simple system with which to tailor the interfacial properties of metals, metal oxides, and semiconductors [8]. There are a number of head groups that bind to specific metals, metal oxides, and semiconductors. The adsorption of alkanethiols on gold [6, 9], silver [10, 11], copper [10], palladium [12, 13], platinum [14], and mercury [15] were investigated. The high affinity of thiols for the surfaces of noble and coinage metals makes it possible to generate well-defined organic surfaces with useful and highly alterable chemical functionalities displayed at the exposed interface [6, 7]. The early literature on SAMs (1983-1993) focused largely on the assemblies formed by the adsorption of organosulfur compounds from solution or the vapor phase onto planar metal substrates of gold and silver [10].

Many self-assembly systems have since been investigated, but mono layers of alkanethiolates on gold are probably the most studied SAMs to date. As a substrate for studying SAMs, gold is a standard substrate.

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There are two considerable reasons supporting this idea: (1) gold forms good (but not uniquely well) SAMs and (2) it is historically the most studied. Also there are three characteristics of gold that make it a good choice as a substrate for studying SAMs. First, gold is easy to obtain, both as a thin film and as a colloid. It is straight forward to prepare thin films of gold by physical vapor deposition, sputtering, or electro deposition. Although expensive and not essential to most studies of SAMs, single crystals are available commercially. Second, gold is exceptionally easy to pattern by a combination of lithographic tools (photolithography, micromachining, others) and chemical etchants. Third, gold is a reasonably inert metal: it does not oxidize at temperatures below its melting point; it does not react with atmospheric O<sub>2</sub>; it does not react with most chemicals [1-4].

The stabilization of the gold nanoparticles with alkanethiols was first reported in 1993 by Mulvaney and Giersig, who showed the possibility of using thiols of different chain lengths and their analysis [16]. Smaller organic soluble gold nanoparticles are prepared via sodium borohydride reduction in a two-phase procedure carried out in the presence of octylammonium bromide (TOAB) [17].

Brust et al. extended this synthesis to *p*-mercaptophenol-stabilized gold nanoparticles in a single phase system [18], which opened an avenue to the synthesis of the gold MPNs stabilized by a variety of functional thiol ligands [17-19]. Murray et al. reported and studied the place-exchange reaction of a controlled proportion of thiol ligands by various functional thiols [20, 21] and the subsequent reactions of these functional MPNs [21, 22].

Understanding reactivity of the gold MPNs and developing efficient strategies to functionalize them is an important key to their application in areas such as catalysis and chemical sensing. Performing reactions on MPNs allows us to tune the properties of surface at the molecular level, but due to the nature of MPNs the choice of reaction is important.

Toward this end, several methods such as ligand place-exchanges (to form poly, homo and hetero functionalized MPNs) [20], nucleophilic substitutions [21], and ester and amide couplings have been investigated.

UV-Vis spectroscopy can improve the size determination of the AuMPNs using Mie Theory [25,26], the UV-Vis and IR spectra provide an

identification of the ligand that is also confirmed by NMR spectroscopy, except that the ligand atoms close to the core give broad signals. [24].

For sufficiently small particles with complex refractive index *m*, scattering is negligible and absorption is proportional to mass path only, irrespective of particle size, according to Mie theory. Size determination of Gold nanoparticles using Mie theory and extinction spectra, measuring the wavelength of the absorption peak interested in the peaks that occur at wavelengths longer than 500 nm and will use these values as model the extinction spectrum in MiePlot. All the numerous subsequent and recent reports correlate the spectroscopic behavior of AuNPs with the Mie theory [25,26]. The main characteristics of the surface plasmon bands are (i) its position around 520 nm; (ii) its sharp decrease with decreasing core size for AuNPs with 1.4-3.2 nm core diameters due to the onset of quantum size effects that become important for particles with core sizes <3 nm in diameter and (iii) steplike spectral structures indicating transitions to the discrete unoccupied levels of the conduction band with monodispersed AuNPs with core diameters between 1.1 and 1.9 nm [26,27].

Thus, the surface plasmon band is absent for AuNPs with core diameter less than 2 nm, as well as for bulk gold. For AuNPs of mean diameter of 9, 15, 22, 48, and 99 nm, the surface plasmon band maximum  $\lambda_{max}$  was observed at 517, 520, 521, 533, and 575 nm, respectively, in aqueous media [24].

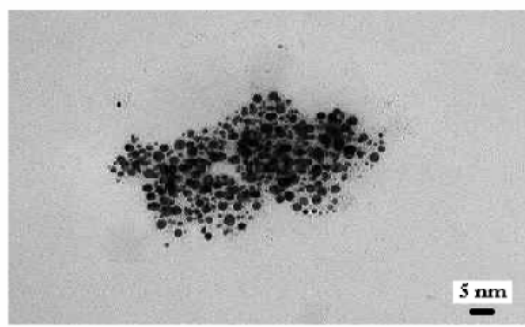
### Results and Discussion:

Primary nanoparticle was prepared following a route reported by Brust and Murray and featured an average core diameter of ca. 2.0 nm as shown in figure 1.

Transmission electron microscopy (TEM) was used to determine the nano scale structure of these aggregates and was carried out on a Philips CN200SEG.

Alkanthiolate of the gold nanoparticle was done following the procedures of Brust and Murray as mentioned, resulting in the formation of a thin film which was washed until it was shown to be pure according to the <sup>1</sup>H NMR spectrum, which showed no signs of alkane thiol, or tetra octyl ammonium bromide.

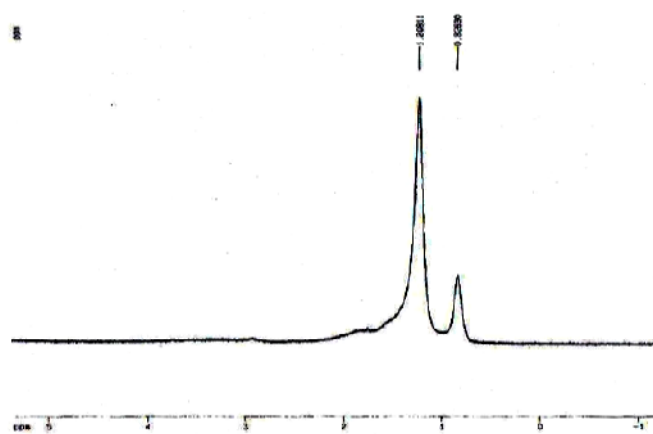
SAMs (self assembled of mono layers) of thiolate compounds on gold surfaces can be formed through the chemical reaction of the S-H bond of the thiol.



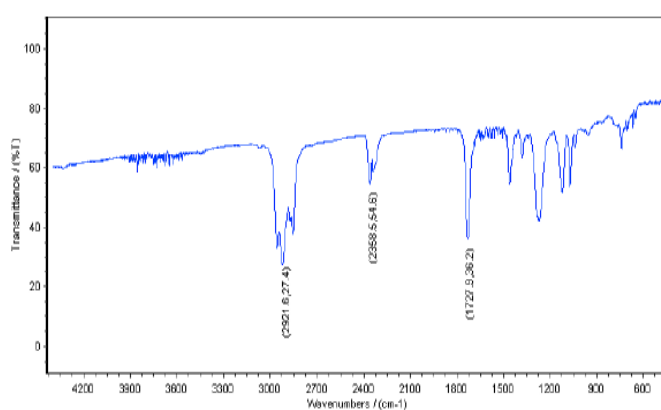
**Fig. 1:** TEM analysis of the monitored MPNs with a core diameter of 2 nm.

The  $^1\text{H}$  NMR spectrum of the C<sub>8</sub>MPN has only broad resonances at 0.8 ppm attributed to the protons on the terminal methyl group and 1.2 ppm attributed to the methylene protons along the alkane thiolate chain (Figure 2a).

The FT-IR spectra of C<sub>8</sub>MPN has 2921.6  $\text{cm}^{-1}$  (C-H, stretching) 2358.5  $\text{cm}^{-1}$  (CH<sub>3</sub>, bending), 1500  $\text{cm}^{-1}$  (CH<sub>2</sub>, bending) (Figure 2b).



(a)



(b)

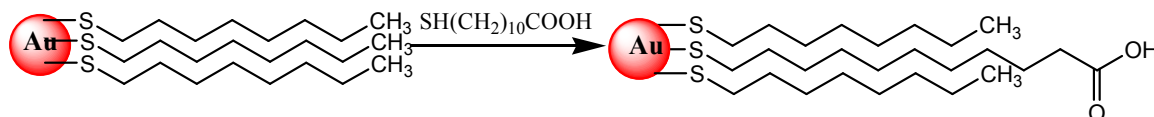
**Fig. 2:**  $^1\text{H}$  NMR (a) and FT-IR (b) spectra of C<sub>8</sub>MPN

The primary MPN stabilized with octanethiolate protected gold nanoparticles (C<sub>8</sub>MPN), were modified

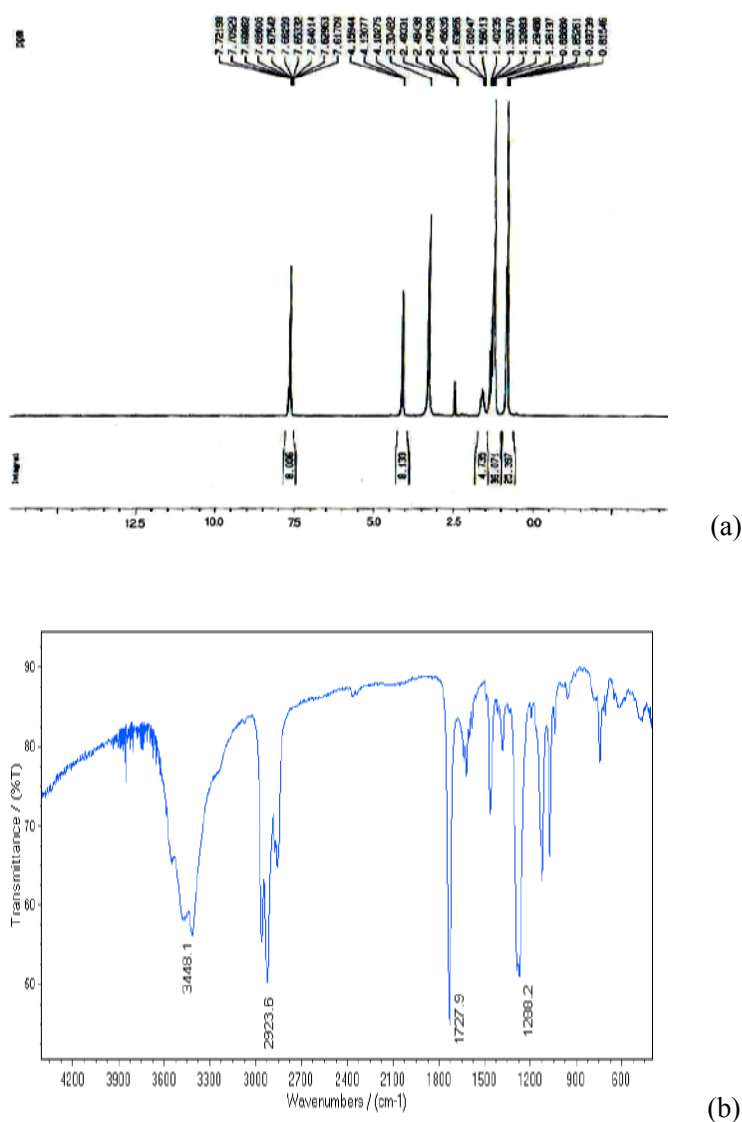
with the procedure which used 11-mercaptoundecanoic acid to form the hydroxyl group

on the surface of the gold nanoparticles. The ligand place exchange route used to form functionalized MPNs.  $^1\text{H}$  NMR spectroscopy and FT-IR spectra

showed the solution free of any non-bonded thiol or 11- mercaptoundecanoic acid ligands.



**Scheme 1.** Modification of octanthiolate protected gold nanoparticle ( $\text{C}_8\text{MPN}$ ) by 11- mercaptoundecanoic acid via ligand place exchange procedure



**Fig. 3:**  $^1\text{H}$  NMR (a) and FT-IR (b) spectra of  $\text{MC}_8\text{MPN}$

The  $^1\text{H}$  NMR spectrum of the modified  $\text{C}_8\text{MPN}$  ( $\text{MC}_8\text{MPN}$ ) has broad resonances at 0.8 ppm attributed to the protons on the terminal methyl group

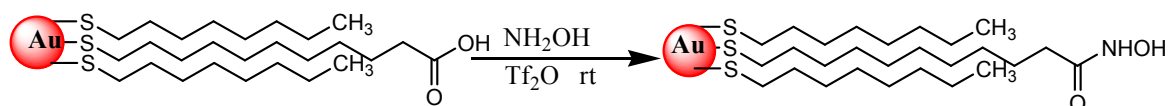
and 1.2 ppm attributed to the methylene protons along the alkanethiolate chain, the 1.62 ppm attributed to the methylene protons next to the carbonyl group, and 7.6

ppm attributed to the proton of hydroxyl group, 2.5 and 3.3 ppm sharp peaks are attributed to H<sub>2</sub>O and DMSO, respectively. The 4 ppm peak attributed to impurity of materials and the 7.5 ppm sharp peak attributed to chloroform which is used with DMSO as second solvent. (Figure 3a).

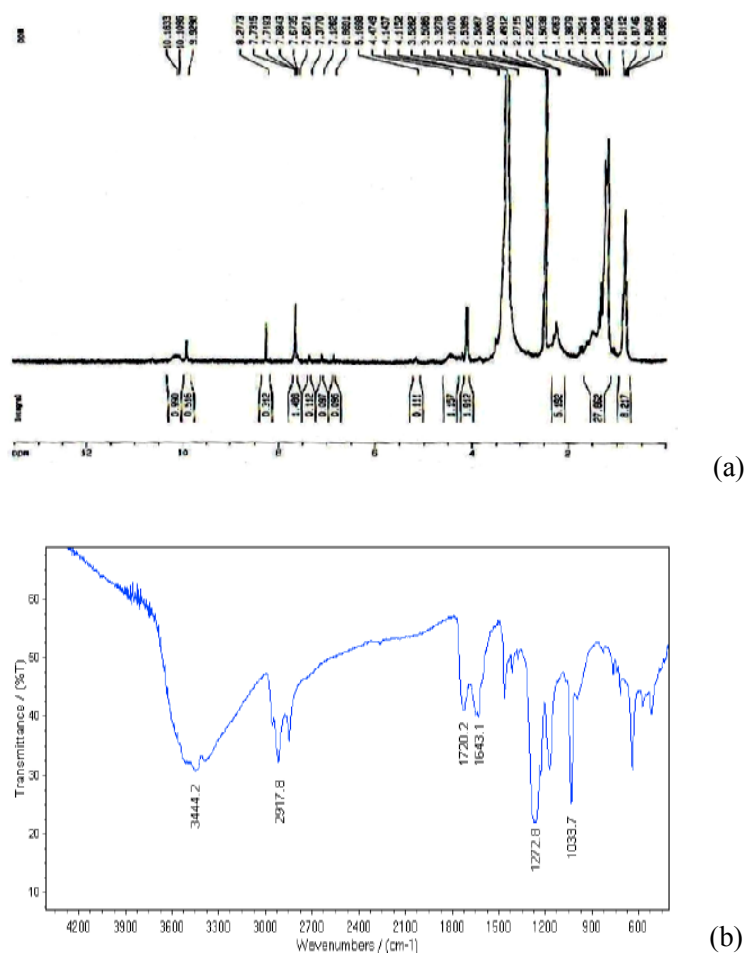
The FT-IR spectra of MC<sub>8</sub>MPN has 3448 cm<sup>-1</sup> (OH of carboxylic group) 2923.6 cm<sup>-1</sup> (C-H, stretching),

1727.9 cm<sup>-1</sup> (carbonyl group), 1600 cm<sup>-1</sup> (CH<sub>3</sub>, bending), 1500 cm<sup>-1</sup> (CH<sub>2</sub>, bending), 1288.2 cm<sup>-1</sup> (C-O, stretching) (Figure 3b).

The obtained gold MPNs (MC<sub>8</sub>MPN) were modified with hydroxyl ammonium chloride to increase the capability of nanoparticles in reaction with metal ligands to form metal complexes as chemical sensors.



**Scheme 2.** Modification of MC<sub>8</sub>MPN by hydroxyl ammonium chloride



**Fig. 4:** <sup>1</sup>H NMR (a) and FT-IR (b) spectra of M<sub>2</sub>C<sub>8</sub>MPN

The <sup>1</sup>H NMR spectrum of the modified M<sub>2</sub>C<sub>8</sub>MPN has broad resonances at 0.91 ppm attributed to the protons on the terminal methyl group and 1.23 ppm attributed to the methylene protons along the alkanethiolate

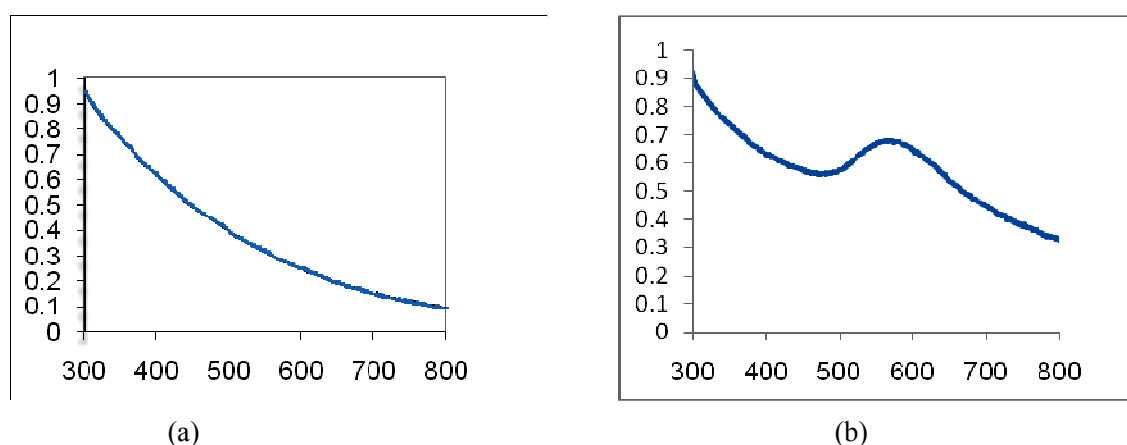
chain, the 2.5 ppm attributed to the methylene protons next to the carbonyl group, and 7.67 ppm attributed to the proton of hydroxyl group, 9.9 ppm attributed to the proton of N-H group. The 2.7 and 3.3 ppm sharp peaks

are attributed to H<sub>2</sub>O and DMSO, respectively. The 4.14 ppm and 8.3 ppm peaks are attributed to impurity of materials (Figure 4a).

The FT-IR spectra of M2C<sub>8</sub>MPN has 3444 cm<sup>-1</sup> (N-H, stretching) 2917 cm<sup>-1</sup> (C-H, stretching), 1720 cm<sup>-1</sup> (carbonyl group near NH), 1643 cm<sup>-1</sup> (N-H, bending) 1272 cm<sup>-1</sup> (CH<sub>3</sub>, bending), 1200 cm<sup>-1</sup> (CH<sub>2</sub>, bending), 1033 cm<sup>-1</sup> (C-N, stretching) (Figure 4b).

The last obtained gold nanoparticles are more able to bond with metals as a ligand in formation of chemical sensors as investigated by using iron (II) because of its known ability to form stable hexa coordinate

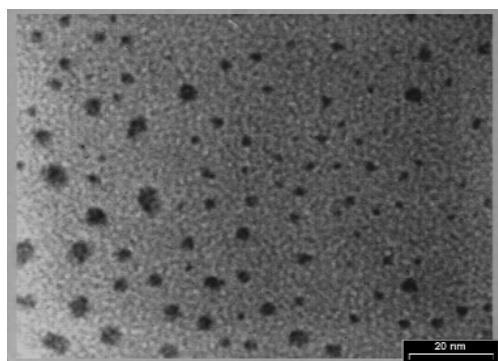
complexes. The Coordination of the modified C<sub>8</sub>MPN to the iron was monitored by UV-vis spectroscopy. Following the formation of the distinctive Fe(H<sub>2</sub>O)<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub>, absorption band (500-600 nm) located beneath the surface plasmon resonance band of the particle, as Fe(H<sub>2</sub>O)<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub> was added to a solution of the modified gold nanoparticles resulting the change of solution color (Figure 5). TEM was used to determine the nanoscale structure of these aggregates. The core diameter of ca. 2.0 nm increased to 5 nm by iron (II) addition as shown in figure 6.



**Fig. 5:** Changes in the UV-Vis spectrum of a CHCl<sub>3</sub> solution of M2C<sub>8</sub>MPN ( $5 \times 10^{-7}$  M) as a (1:3) MeOH/CHCl<sub>3</sub> solution of Fe(H<sub>2</sub>O)<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub> ( $2.5 \times 10^{-3}$  M) is added. (a) Before metal addition. (b) after metal addition.

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increased to 5 nm by iron (II) addition as shown in Figure 6.



**Fig. 6:** TEM analysis of thiol functionalized gold nanoparticles with a core diameter of 5 nm.

### Conclusions

Understanding reactivities of the gold MPNs and developing efficient strategies to functionalize them is

an important key to their application in areas such as catalysis and chemical sensing. It is more convenient to use a number of standard SAMs or MPNs and

subsequently perform reactions on MPNs to modify the surface chemistry.

In summary, we have shown that gold nanoparticle aggregations can be facilitated by transition metals coupled with alkanthiolate MPNs. The modified alkanthiolate MPNs have the capability to coordinate metals, generation of various nano composites or to bond with metals as a ligand in formation of chemical sensors. Preparation of metal complexes set the stage to investigate the metal-mediated assembly of the nanoparticles.

### Experimental

The compounds octanethiol, dodecanethiol, hydrogen tetrachloroaurate (III)  $\text{HAuCl}_4$ , tetra octyl ammonium bromide, sodium borohydride, 11-mercaptoundecanoic acid, hydroxyl ammonium chloride,  $\text{Tf}_2\text{O}$ , thionyl chloride were all purchased from Aldrich and Merck used as received. Acetone, acetonitrile, dichloromethane, toluene, methanol, diethyl ether and hexane, ethanol (both anhydrous and 95 %) were used, and silica gel was purchased from EM Science.

Following the procedures of Brust [17, 18] and Murray [22], to a 250 mL round bottom flask was added hydrogen tetra chloroaurate (III) trihydrate (0.30 g, 0.768 mmol) dissolved in 28 mL distilled water (resulting in a bright yellow solution) and tetra octyl ammonium bromide (2.01g, 3.69 mmol) dissolved in 70 mL toluene (a clear and colorless solution). The contents of the flask were rapidly stirred for 30 min at room temperature in order to facilitate phase transfer of the hydrogen tetrachloroaurate (III) trihydrate into the toluene layer, which resulted in the organic layer turning to a dark orange color and the aqueous layer becoming clear and colorless. After phase transfer the aqueous layer was removed and the appropriate alkanethiol (ca. 2.3 mmol) was added to the solution via a volumetric pipette and then cooled to 0 °C while a fresh solution of sodium borohydride (0.33 g, 8.68 mmol) in 18 mL water was prepared. The aqueous sodium borohydride was added to the cold toluene solution over ~5 seconds and the mixture was allowed to stir overnight as it warmed to room temperature (~18 hours). The organic layer was washed with 3 x 20 mL distilled water, dried with  $\text{MgSO}_4$  and concentrated. The concentrated MPN was then suspended in 200 mL of 95 % ethanol and placed in the freezer overnight during which time the  $\text{C}_8\text{MPN}$  precipitated from solution. The ethanol was then decanted and the MPN was dissolved in benzene and concentrated once again resulting in the formation of a film in the round bottom flask. This film was washed

repeatedly with  $10 \times 15$  mL of 95% ethanol. The  $\text{C}_8\text{MPN}$  was washed this way until it was shown to be pure according to the  $^1\text{H}$  NMR spectrum, which showed no signs of alkanethiol, dialkyl disulfide or tetra octyl ammonium bromide.

11-mercaptoundecanoic acid and hydroxyl ammonium chloride were used for modification of the synthesized nanoparticles. The modified MPN was prepared by dissolving 1 mmol of the  $\text{C}_8\text{MPN}$  in 20 mL of chloroform and then 2 mmol of 11-mercaptoundecanoic acid was added and the mixture was stirred for 35 minutes. The resulting  $\text{MC}_8\text{MPNs}$  was concentrated and washed copiously with acetonitril.  $^1\text{H}$  NMR spectra show the purity of the prepared  $\text{MC}_8\text{MPNs}$  from any unreacted thiols. The obtained gold  $\text{MC}_8\text{MPNs}$  were modified with the hydroxyl ammonium chloride to increase the capability of nanoparticles in reaction with metal ligands to form metal complexes; the next modified MPNs was prepared by dissolving 1 mmol of the hydroxyl ammonium chloride and 1 mmol sodium hydroxide in 30 mL of ethanol and refluxing the mixture for 1 hour. 1 mmol of  $\text{MC}_8\text{MPNs}$  was added to 1.5 mmol of  $\text{Tf}_2\text{O}$  [23], and was stirred for 10 minutes and then was added to the first solution. The resulting  $\text{M}_2\text{MC}_8\text{MPN}$  was concentrated and washed copiously with acetonitril.  $^1\text{H}$  NMR spectra show the purity of the prepared  $\text{M}_2\text{MC}_8\text{MPNs}$  from any unreacted materials.

To investigate the formation of metal complexes, iron (II) was used because of its known ability to form stable hexa coordinate complexes. For this purpose a  $\text{CHCl}_3$  solution of  $\text{M}_2\text{MC}_8\text{MPNs}$  with the concentration of ( $5 \times 10^{-7}$  M) and a (1:3)  $\text{MeOH}/\text{CHCl}_3$  solution of  $\text{Fe}(\text{H}_2\text{O})_6(\text{BF}_4)_2$  with the concentration of ( $2.5 \times 10^{-3}$  M) are prepared [2]. The Coordination of the modified  $\text{C}_8\text{MPN}$  to the iron was monitored by UV-vis spectroscopy. Preparation of metal complexes set the stage to investigate the metal-mediated assembly of the nanoparticles.

Transmission electron microscopy (TEM) was used to determine the nano scale structure of these aggregates and was carried out on a Philips CN200SEG.

$^1\text{H}$  NMR spectra were recorded on a Bruker Avance (200 MHz) spectrometer. UV-Visible absorption spectra were recorded on a Rayleigh UV 1600.

FT-IR spectra were recorded on a Rayleigh WQF-510 spectrometer on KCl plates and are reported in wave numbers ( $\text{cm}^{-1}$ ).

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