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One-pot synthesis of sub-3 nm gold nanoparticle networks connected by thio-based multidentate fullerene adducts

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A new organo-soluble [60]fullerene hexaadduct bearing twelve thiocyanate functions has been synthetized and successfully used as a stabilizing/assembling agent to assemble homogeneous sub-3 nm gold nanoparticles into extended tridimensional networks.

One of the biggest challenge in nanotechnology is to control the self-assembly of interconnected nanoparticles at the microscopic scale.[1] Gold nanoparticles (AuNPs) are among the most widely used nanomaterials due to their easy synthesis, great stability, low toxicity and promising applications in electronics, photonics, medicine and catalysis.[2] Several studies have shown that fully organized AuNPs with narrow size-dispersion can be obtained in self-assembled architectures incorporating macromolecules.[3] For example, DNA has been widely employed in the elaboration of long range ordered materials but the cost, the low scale availability and the necessity to use physiological media are major drawbacks. Other routes are based on the use of multidentate organic linkers in order to connect particles and try to direct the assembly by either direct synthesis or coupling reactions from functionalized AuNPs.[4] Nevertheless, all studies reported so far with these methods involve large particles with a diameter above 5 nm. The assembly of AuNPs with functionalized fullerene nodes through weak electrostatic interactions has also been done and led to particles larger than 8 nm.[5] Thus, the preparation of 3D-networks incorporating smaller AuNPs remains a challenge. This is particularly important for their future application in the field of catalysis.[6] In this paper, we show that the use of a bulky organic 3D-linker, namely a C_{60} hexaadduct,[7] is perfectly suited for the one-pot synthesis of hybrid materials where homogeneous sub-3 nm AuNPs are connected through strong S-Au bonds.

Since the first synthesis described by Brust *et al.*, thiol derivatives have been considered as stabilizing agents of choice for AuNPs synthesis.[8] But many studies have shown that these ligands are often too unstable and may be easily oxidized into disulfide analogues.[9] Ciszek *et al.* have demonstrated that gold nanomaterials can also be obtained by using thiocyanate precursors.[10] Indeed thiocyanate derivatives possess a greater stability against oxidation and may act as protecting groups of thiol functions before grafting on a gold surface. During the formation of the material, thiocyanate functions are generally reduced by a surface mediated process resulting in the spontaneous cleavage of S-CN bonds and formation of strong Au-S interactions. On the other hand, drastic reducing conditions used for AuNPs synthesis (borohydride) can also give rise

to the *in situ* transformation of thiocyanates into the corresponding thiolates.[11] Based on these observations, we decided to study the one-pot synthesis of AuNPs starting from a C_{60} hexaadduct derivate bearing twelve peripheral thiocyanate groups. The synthesis of the fullerene hexaadduct ligand is depicted in Scheme 1. Treatment of malonate **1**[12] with KSCN in EtOH/H_2O afforded malonate **2**. Fullerene hexakis-adduct **3** was then prepared by the one-pot reaction of C_{60} with **2** under the conditions reported by Sun.[13] The reaction is performed under thermodynamic conditions thus allowing a control of the regiochemistry. The reaction of C_{60} with **2** in the presence CBr_4 and DBU provided the T_h-symmetrical hexa-adduct **3**. All of the spectroscopic studies results were consistent with the proposed molecular structure (see ESI).
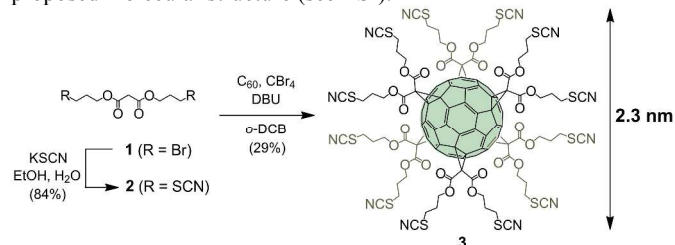
Scheme 1 Synthesis of **3** (the diameter of *ca.* 2.3 nm corresponds to the S to S distance of addends located at opposite poles of the C_{60} core).

The preparation of AuNPs by the simultaneous reduction of both the gold(III) precursor and the terminal thiocyanate groups of **3** is an interesting synthetic challenge owing to the attendant problem resulting from the presence of the reducible ester functions in **3**. Indeed, treatment of a model fullerene hexa-adduct with six diethylmalonate addends revealed that the ester functions are not reactive in the presence of a large excess of $LiBH_4$ (20 eq.) in THF as long as the temperature is kept below 10°C. Under similar conditions ($LiBH_4$, THF, 0°C), **3** is slowly consumed. However, its transformation into the corresponding dodecathiol could not be achieved in a clean manner. Actually, only partially reduced products were obtained by performing the reduction at 0°C. These first preliminary investigations revealed however that compound **3** is a suitable building block for the construction of AuNP networks under reductive conditions. The synthetic route selected for the preparation of the AuNPs consists in a simultaneous addition (1 ml.min^{-1}) of THF solutions of the gold precursor ($HAuCl_4$) and the reducing agent ($LiBH_4$) to a THF solution of **3** cooled at 0°C. In our first experiments, 4-aminothiophenol (HATP) was also introduced in

the medium as a secondary stabilizing agent. Indeed ultra-small cluster $Au_{25}(ATP)_{17}$ has recently been prepared in our group by using the same experimental approach.[14] Thus, this secondary stabilizing agent was added to the reaction mixture to check if both ligand can coexist within the material and if the size of particles can be tuned by adding a smaller ligand (see detailed synthetic procedure in ESI). AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$] and AuNP@[(**3**)$_{1/5}$(ATP)$_{1.5}$] compounds have been synthetized by mixing 1.5 eq. of ATP (equivalent compared to gold) with 1/11 eq. and 1/5 eq. of **3** respectively, whereas AuNP@[(**3**)$_{1/11}$] and AuNP@[(**3**)$_{1/5}$] have been obtained only by introducing 1/11 eq. and 1/5 eq. of **3** respectively in the reaction medium. For each experiment, an insoluble black powder is obtained owing to aggregation of AuNPs. The isolated materials have been obtained in relative high yields (up to 57 % based on Au) and were characterized in solid state by PXRD, TGA, MET and spectroscopic techniques.
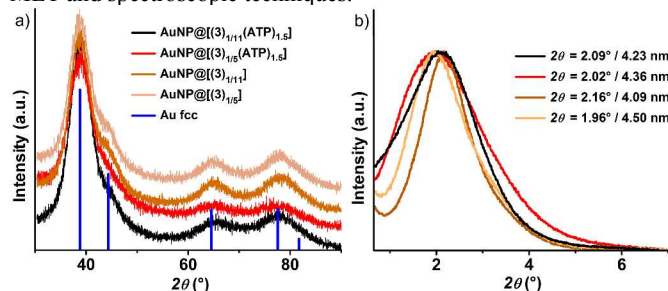

Fig. 1 Powder XRD patterns a) in the 2θ = 30-90° range and b) in the 2θ = 0.45-7° range.

Wide angles powder XRD patterns (Fig. 1a) reveal that all samples present characteristic diffraction peaks of cubic face centered gold at 38, 44, 64 and 77° (2θ) for (111), (200), (220) and (311) reflections, respectively. The relative broadness of these peaks is directly correlated with the size of particles according to the Debye-Scherrer method and suggests the presence of small AuNPs. As already described in previous studies,[14,15] an intense diffraction peak centered at small angles ($2\theta \approx$ 1.9-2.2°) is observed for each material (Fig. 1b). This contribution is attributed to a periodic center-to-center distance between AuNPs, and thereby to a short-ranged organization ($d \approx$ 4.1-4.5 nm according to Bragg's law) (Table 1). Consequently the presence of this diffraction peak at low angle points out that the system is highly homogeneous, meaning that the AuNPs diameter is well defined and the interparticular space distance is constant so there is no aggregation of the organic molecules. Thus we can deduce that AuNPs are effectively self-assembled within the material. It is noteworthy that samples incorporating only fullerene adducts present a sharper diffraction peak in this area, which can be attributed to a better homogeneity of the material. Furthermore the presence of ATP molecules do not seem necessary for the AuNPs formation and the self-assembling process, thus showing that the aggregation is mainly directed by multidentate fullerene core units.
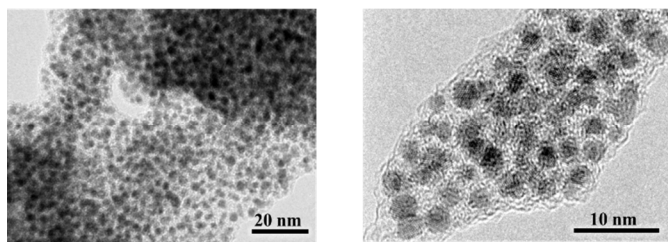

Fig. 2 TEM micrographs of AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$].

Table 1 Center-to-center (C-to-C) distances extracted from TEM and PXRD data, AuNPs diameter obtained by TEM experiments and deduced interparticular distances.

	C-to-C (nm) from PXRD	AuNPs diameter (nm) from TEM	C-to-C (nm) from TEM	Interparticular distances (nm)
AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$]	≈ 4.2	1.9 ± 0.9	4.0 ± 1.0	≈ 2.3
AuNP@[(**3**)$_{1/5}$(ATP)$_{1.5}$]	≈ 4.4	2.1 ± 0.5	4.3 ± 1.1	≈ 2.3
AuNP@[(**3**)$_{1/11}$]	≈ 4.1	2.5 ± 0.5	3.6 ± 0.6	≈ 1.6
AuNP@[(**3**)$_{1/5}$]	≈ 4.5	2.5 ± 0.5	4.4 ± 0.6	≈ 2.0

TEM micrographs show that these materials are made of spherical and homogeneous small AuNPs densely packed together (Fig. 2 and Fig. S5-S8). Samples incorporating ATP present AuNPs with an average diameter of 2 nm, whereas other samples are characterized by a slightly larger diameter close to 2.5 nm (Table 1). The small difference in AuNPs diameter between those samples may be explained by the faster reactivity of the small and monodentate ATP for the particles growth when compared to the bulky multitdentate C_{60} derivative. In addition, we can see that the concentration of fullerene molecules in the reaction has no influence on the size of particles. Center-to-center AuNPs distances have also been measured from TEM images (Fig. S5-S8) and are in good agreement with those determined by XRD experiments at small angles scattering (Table 1). From the center-to-center AuNPs distances obtained by PXRD, which are more accurate due to the problem of AuNPs overlapping on TEM images, and the AuNPs diameter evaluated by TEM, we deduced the interparticular distances of samples (Table 1). These distances vary from 1.6 to 2.3 nm. Those values correspond well to the diameter of the functionalized C_{60} branching core unit which is of 1.6 nm when the external functions are bent and 2.3 nm when they are extended, confirming that the interparticular space is occupied by one layer of the C_{60} moieties. From TEM images, the size of **3**@AuNPs aggregates goes up to 400 nm, pointing out the good capability of fullerene derivative **3** to interconnect AuNPs over a long distance.
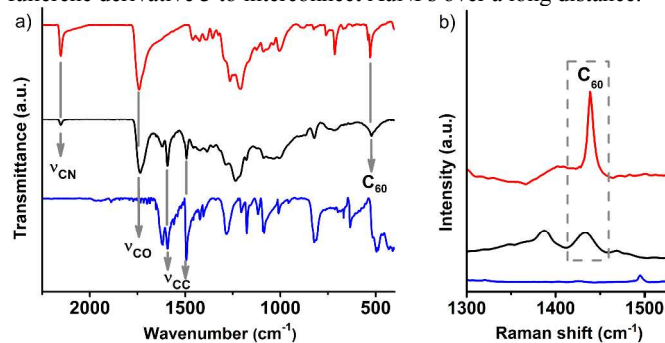

Fig. 3 a) FTIR and b) Raman spectra of AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$] (black), **3** (red) and ATP (blue).

From TGA experiments the weight loss corresponding to the organic parts goes from 40 to 73 % depending on the ratio of ligand and gold used for the synthesis and the presence of the ATP molecules (Fig. S9). For all the samples, FTIR spectroscopy confirmed the presence of the hexasubstituted fullerene moiety by the observation of the most intense T_{1u} band located at 526 cm^{-1}, which is characteristic for C_{60} core (Fig. 3a for AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$], Fig. S10-S11 for other samples).[16a-b] The presence of the ν_{CO} stretching band at 1729 cm^{-1} confirmed that ester functions have not been affected during the preparation of the AuNPs. In contrast, the intensity of the ν_{CN} band of thiocyanates at 2152 cm^{-1} has drastically decreased when compared to the starting ligand **3**. This observation corroborates the partial reduction of thiocyanate functions and the formation of Au-S bonds. The presence of ATP in the respective experiments has been also confirmed by the additional observation of aromatic ν_{CC} vibration bands at 1591 and 1493 cm^{-1}. Raman spectroscopy also validates the presence of fullerene hexaadducts for AuNP@[(**3**)$_{1/11}$(ATP)$_{1.5}$]. Indeed the starting compound **3** is characterized by an intense A_g(2) vibration band at 1438 cm^{-1} which is attributed to fullerene-based derivates,[16c] and the same band is observed with a loss of intensity

and red-shifted at 1431 cm^{-1} when compound **3** is connected to AuNPs (Fig. 3b).

X-ray photoelectron spectroscopy (XPS) on AuNP@[(**3**)$_{1/11}$] was used in order to understand the interactions between AuNPs and the branching fullerene units. Fig. 4 shows XPS spectra of the S 2p, N 1s, C 1s and Au 4f core levels obtained from AuNP@[(**3**)$_{1/11}$]. The S 2p peaks (Fig. 4a) can be fit with four contributions. The one located at ≈ 162.2 eV is attributable to the cleavage of S-CN bonds and thus the formation of gold thiolate interactions. The contribution at ≈ 163.4 eV is attributed to unbound thiols. Their presence can be explained by direct reduction of thiocyanates in presence of LiBH$_4$.[11] Remaining thiocyanates functions are still localized at ≈ 164.8 eV, thus showing that the reduction process is not complete.[17] An additional signal above 168 eV is observed and is generally attributed to oxidized sulfur contamination.[18]
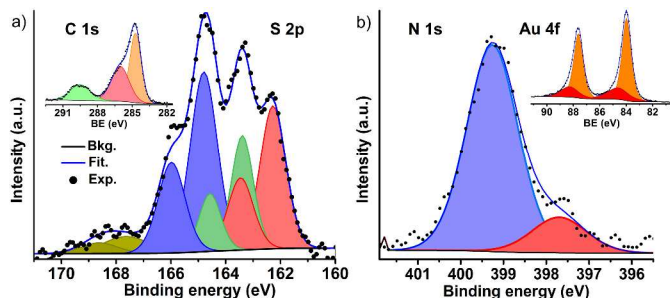

Fig. 4 XPS spectra of a) S 2p (inset C 1s) and b) N 1s (inset Au 4f) on AuNP@[(**3**)$_{1/11}$].

Fig. 4b shows core level spectra of N 1s which can be fit with two contributions at ≈ 399.3 and ≈ 397.9 eV respectively. The first one and more intense is attributed to remaining free thiocyanate functions whereas the second one can be assigned to CN groups adsorbed on the gold surface, validating the cleavage of S-CN bounds.[10b, 17c]

The C1s spectrum (inset Fig. 4a) exhibits three contributions at ≈ 284.8, ≈ 286.0 and ≈ 289.5 eV respectively which have been attributed to CC, CO and the last to carboxyl groups. These binding energies are in good agreement with fullerene derivatives bearing ester functions.[19]

Au 4f core level spectrum (inset Fig. 4b) shows the presence of two contributions. The first contribution at ≈ 84.0 eV is largely predominant and attributable to Au^0 present in gold core of nanoparticles, and the last located at ≈ 85.2 eV have already been observed by other groups,[20] and is attributed to gold surface atoms of particles interacting with thiolate groups.

In conclusion, we synthetized a new fullerene hexaakis adduct **3** incorporating twelve thiocyanate functions on its surface. Coupling this 3D organic linker and thiocyanate external functions with a one-pot synthesis involving LiBH$_4$ as a reducing agent, we obtained *in-situ* the formation of sub-3nm AuNPs and their assembly into a 3D-network. Different techniques used for in-depth characterizations of the materials reveal that the AuNPs size is homogeneous, that they are connected through strong Au-S bonds and that the interparticular space is occupied by only one layer of C$_{60}$ moieties. This association of ultra-small AuNPs with a carbon-based organic linker in one network makes this kind of hybrid material promising as catalyst with potential synergetic effects between the two parts. By selecting well-designed organic linkers with the appropriated external functions and well-adapted synthesis, the formation of robust and organized 3D-network of small nanoparticles should be soon possible.

Notes and reference

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