Platinum colloids stabilized by bifunctional ligands : self-organization and connection to gold†

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Platinum nanoparticles accomodating bifunctional thiolate ligands self-assemble into regular superstructures or organize around a large gold particle; the shape of the superstructures can be modulated by addition of water.

There is presently a substantial interest for the study and the use of the novel properties of metal nanoparticles.[1] Complexation of ligands at the surface of the nanoparticles may allow a good control of both their physical and chemical properties.[2] Furthermore, the use of polyfunctional ligands may lead to connection between particles, to their self-assembly and the formation of monolayers on surfaces, as recently described.[1g,3,4] However, the coordination chemistry of the surface of nanoparticles has been relatively little developed, probably because of the lack of adequate methods for synthesizing particles of controlled surface state. CO coordination at the surface of metal particles has often been used as a probe of the surface state[5] whereas thiol or amine coordination has been used to stabilize metal particles.

In our group, we have been interested for some time in the synthesis of metal nanoparticles from organometallic precursors.[6] Two main reasons for this interest were the possibilities to access to monodisperse particles of very small size (1–2 nm) and to perform coordination chemistry at their surface. In this respect, we have been able to prepare platinum particles of small size (*ca.* 1.5 nm) protected by various ligands such as CO, THF, PPh₃, TOPO (trioctylphosphine oxide), thiols and amines. In the presence of thiols, we have shown the absence of ligand exchange at the NMR time scale between free and complexed thiol.[6c–f]

Having demonstrated the possibility to control the growth and the stability of nanoparticles with ligands, the next step is the organization of the particles in two or three dimensions. This can be achieved by self-organization (In/TOPO[6e]) or by connection of the particles in a way similar to that used in molecular techtonics.[7] We report in this communication our first attempts in this direction using both the coordination ability of dithiols and the formation of hydrogen bonded networks.

The reaction of Pt₂(dba)₃ with CO (1 bar) in THF leads to the formation of platinum nanoparticles of uniform size centered near 1.2 nm (colloid **1**). Addition of alkanedithiol ligands proceeds similarly as previously described for octanethiol,[6c] and leads to new platinum particles (alkane = propane, colloid **2a**; octane, colloid **2b**). The reaction can be followed by IR spectroscopy in which a shift to lower frequency of surface CO stretches is observed from 2050, 1808 cm⁻¹ to 2046, *ca.* 1800 cm⁻¹ upon addition of 0.1 eq./Pt dithiol. The particles have been characterized by HREM and, for some samples, by WAXS (wide angle X-ray scattering) which both demonstrate their fcc structure. Their mean size is *ca.* 1.6 nm, similar to octanethiol stabilized particles.[6c] However, in contrast to the results

observed with octanethiol, the particles agglomerate into large superstructures which do not evidence any crystalline arrangement but in which the inter-particle distances is regular (Scheme 1; experimental and characterization details are given as ESI†).

In order to determine whether this aggregation was due to the presence of coordination links between the particles, a solution of colloid **2b** was reacted with large gold particles prepared by the Turkevich method.[8] According to the density of platinum particles, the organization observed around gold particles [concentric circles, Fig. 1(b)] may lead to long range ordering. In each case, a regular inter-particle distance of *ca.* 1 nm can be measured. This result therefore demonstrates the possibility to use a linker for connecting two particles, of different or of same nature.

Another approach for connecting nanoparticles consists in trying to organize them through hydrogen bonds.[9] In our case, we chose to organize platinum nanoparticles by employing bifunctional thiophenol derivatives. As the thiolate groups display high affinity for platinum, the anchoring of the ligands at the surface of the particles occurs through the thiolate functions leaving free the *para* substituents for hydrogen bonding. This leads to a new series of platinum particles accommodating respectively *p*-hydroxythiophenol (colloid **3a**), *p*-aminothiophenol (colloid **3b**), and *p*-mercaptobenzoic acid (colloid **3c**). The addition of each ligand to compound **1** can be followed as before by IR spectroscopy. The terminal CO stretch shifts upon addition of 0.15 eq./Pt substituted thiophenol to a value of *ca.* 2040 cm⁻¹. The compounds were characterized by microanalysis, TEM and HREM. In all cases, the products were found to consist of severely agglomerated nanoparticles, the
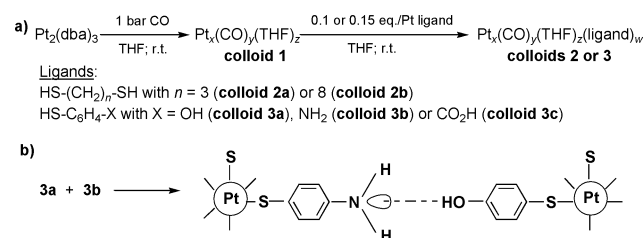
Scheme 1 Synthesis of bifunctional ligand stabilized Pt nanoparticles (a) and [Pt]⁰ self-assemblies (b).
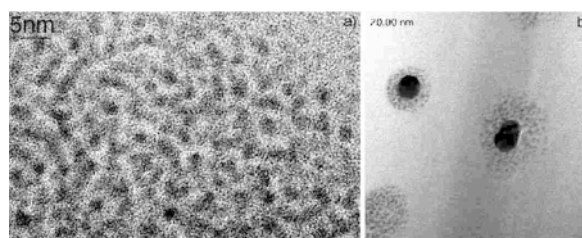

Fig 1 HREM micrograph of Pt particles stabilized by propanedithiol (a) and of [Pt]⁰(S–S)[Au]⁰ assemblies (b).

† Electronic supplementary information (ESI) available: experimental and characterization details; Schemes 1 and 2; Figs. 1–4; Graphical Abstract. See http://www.rsc.org/suppdata/cc/b1/b103781c/
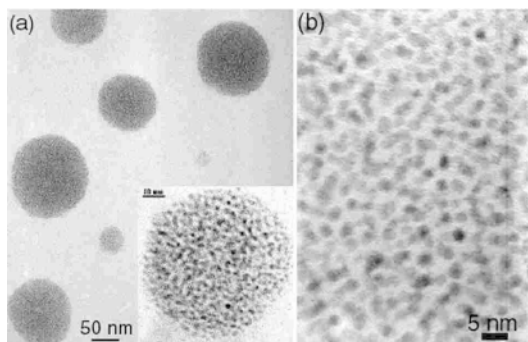
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Fig 2 TEM (a) and HREM (b) micrographs of disks resulting from the condensation of **3a** and **3b** in the presence of water.

distance between which appears regular (near 1.5 nm). In most cases (Fig. 4, ESI†), the agglomerates adopt a compact shape, spherical or distorted spherical as also observed by Boal *et al.*[9] Since water may modify the hydrogen bonding network, the reaction was also carried out in the presence of water. In this case, disks composed of a monolayer of platinum particles were observed [Fig. 2(a)]. HREM analysis of these agglomerates [Fig. 2(b)] shows the presence of well-crystallized fcc platinum particles of uniform size near 1.6 nm, indicating the absence of modification of the particles upon complexation and reaction with water. Similar results were found with compounds **3b** and **3c**. In the latter case, the distance between the particles seems to be slightly shorter (1 nm) which may arise from strong hydrogen bonds between carboxylic groups.

In order to favour the organization of the particles, we mixed together fresh solutions of **3a** and **3b** containing hydroxy and amino pendent groups, respectively. XRD analysis of the samples is in accord with the presence of small fcc platinum with additional peaks at small angles possibly resulting from organization of the particles. TEM micrographs of **3a/3b** evidence the organization of the particles into systems showing an unidirectional anisotropy and resembling nanocrystals (Fig. 3, graphical abstract). Moreover in several cases we observe the formation of nanotubes which are hollow and may accommodate some 'pseudocrystals'. However, HREM analysis demonstrates that the 'pseudocrystals' or the walls of the tubes consist of fcc Pt nanoparticles of intact mean size and structure. As for the superstructures observed with **3a** alone, the addition of water to the system releases the hydrogen bonded network, leading to a monolayer organization.
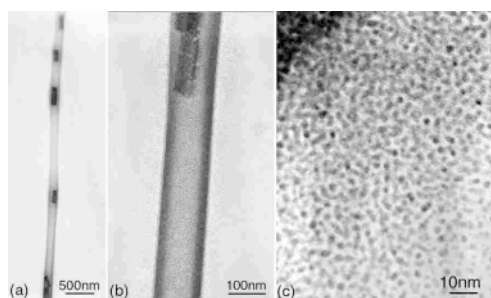

Fig 3 TEM and HREM micrographs of platinum nanotubes at different magnifications (a) ×15000 (b) ×100000 (c) ×600000.

In conclusion, functionalised platinum nanoparticles may be used as individual blocks for the growth of 2D or 3D superstructures through coordination bonds or hydrogen bond-

ing networks. Although the chosen systems are very simple, several points appear nevertheless of interest : (1) the fact that water can control the shape of the hydrogen bonded agglomerates and favours the formation of monolayers is promising as far as the deposition of nanoparticles exhibiting controlled interparticle distance is concerned and may lead to selected electronic measurements or applications; (2) the shape of the obtained agglomerates are not yet predictable but some systems reproducibly display a preferred axis of growth to form 'pseudo-crystals' or nanotubes leading to possible access of nanowires comprised of nanoparticles; (3) connecting nanoparticles appears easy and may lead to interesting chemical and physical properties which will be studied in the future.

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