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Dendrimer-Based Gold Nanoparticles: Syntheses, Characterization and Organization

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UNIVERSITE DE NEUCHATEL

FACULTE DES SCIENCES

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Keywords

Self-organization, nanoparticles, organic inorganic composites, mesophases, ordered dendrimers, mesomorphic dendrimers, metamaterials, metal clusters, optical properties, electrical properties

Mots-clés

Auto-organisation, nanoparticules, composés organiques-inorganiques, mesophases, dendrimères ordrés, dendrimères mésomorphes, métamatériaux, agrégats métalliques, propriétés optiques, propriétés électriques

Abstract

Since the incorporation of gold nanoparticles (AuNPs) in the Lycurgus cup in the 4th century AD allowing a dichroism in reflected and transmitted light, headways paved the path for the synthesis of AuNPs. The optical (surface plasmon resonance) and other properties become size-dependant for small AuNPs (quantum size effect) and can be modulated by controlled synthesis conditions. It is this size dependence that makes nanoparticle-based materials so attractive. But the major breakthrough in terms of synthesis of small AuNPs (about 2 nm) was brought by Brust in 1994. He published a biphasic method that allowed one to obtain alkanethiol-stabilized AuNPs of reduced dispersity. Brust has extended his synthesis in 1995 to *p*-mercaptophenol-stabilized AuNPs (Au/pMP) in a single phase. Both these well-established procedures were used to synthesize the precursor particles we further modified in this study.

It has been shown by calculations that materials with effective negative index of refraction (metamaterials) can be obtained by the three-dimensional organization of metal nanoparticles. The basic idea of this thesis is to use liquid-crystalline dendrimers attached to metal nanoparticles as a vehicle to organize the latter. Therefore the goal of the thesis was the preparation of small, mono-disperse metal nanoparticles and the development of a strategy to covalently bind liquid-crystalline dendrimers. Finally, it was tested if these new composite materials self-assemble in two and three dimensions.

In this study, liquid-crystalline-dendrimer-based gold nanoparticles (Au/LCDs) have been successfully prepared by ligand exchange or esterification. Depending on the nature and the proportion of the grafted molecules (G_0 -mesogen up to G_2 -dendrimer), they exhibit either mesomorphic properties or a self-organization behavior on surfaces at the nanometer scale.

Concerning the synthesis, three different pathways have been used to access these new materials: 1) the direct synthesis of AuNPs using thiolated dendrons by the convenient Brust's biphasique method; 2) the ligand exchange to introduce thiolated dendrons or the

OH moieties to further esterify HOOC–dendrons; 3) the direct esterification of HOOC–dendrons on Au/pMP.

Any of these approaches has its advantages and drawbacks. And finally the esterification of dendrons has appeared to be easy to carry out and has been the method which required the least amount of dendrimers; a default quantity has even allowed one to esterify only a fraction of all the available functional groups.

On the other hand, size exclusion chromatography has been used as an effective purification in the early stages of Au/LCDs syntheses (precursor particle synthesis and ligand exchange) and ultrafiltration in a stirred cell has been found as the fastest and simplest way to yield high purity final dendrimer-based materials.

Concerning the characterization of these particles, a G_0 chiral mesogen as well as a first-generation cyanobiphenyl derivative esterified on Au/pMP have given rise to non-characteristic mesophases. Besides, TEM observations revealed that the first-generation cyanobiphenyl derivative has been able to promote self-organization on a surface when used in a direct synthesis or in an exchange reaction on gold, by esterification on Au/pMP, and in an exchange reaction on silver and palladium particles, although no liquid-crystalline phase was observed for any of these compounds using polarized optical microscopy.

In conclusion, this study has emphasized esterification (in addition to direct synthesis and ligand exchange) as a valuable means to graft liquid-crystalline dendrimers to the shell of small particles with a low polydispersity. Even though only surface organization promoted by dendrons was observed so far, an optimization of synthetic parameters as well as the tuning of the LCDs could undoubtedly allow a better organization and the opportunity to access our aim, metamaterials with their outstanding properties.

Résumé

Depuis l'incorporation de nanoparticules d'or (AuNPs) dans le vase de Lycurgue au 4^{ème} siècle après J.-C., ce qui permet un dichroïsme entre lumière réfléchie et transmise, de nombreuses avancées ont ouvert la voie à la synthèse des AuNPs. Leurs propriétés optiques ainsi que d'autres propriétés deviennent dépendantes de la taille pour les AuNPs de petite dimension et peuvent être modulées par des conditions de synthèse contrôlées. C'est cette dépendance de taille qui rend les matériaux à base de nanoparticules si attrayants. Mais l'avancée majeure en termes de synthèse de petites AuNPs (environ 2 nm) a été réalisée par Brust en 1994. Il a publié une méthode biphasique qui permet d'obtenir des AuNPs de polydispersité réduite stabilisées par des alcanethiols. En 1995, Brust a étendu sa synthèse aux AuNPs stabilisées par du *p*-mercaptophenol (Au/pMP) mais en une seule phase. Ces deux procédures bien établies ont été utilisées pour synthétiser les particules de départ que nous avons ensuite modifiées dans cette étude.

Il a été démontré par des calculs que les matériaux avec un indice de réfraction négatif effectif (métamatériaux) peuvent être obtenus par l'organisation tridimensionnelle de nanoparticules métalliques. L'idée de base de cette thèse est d'utiliser des dendrimères liquides cristallins attachés à des nanoparticules métalliques comme vecteur d'organisation de ces dernières. Par conséquent, l'objectif de la thèse a été la préparation de petites nanoparticules métalliques monodisperses et l'élaboration d'une stratégie visant à lier de manière covalente des dendrimères liquide-cristallins. Enfin, il s'agit de tester si ces nouveaux matériaux composites s'auto-assemblent en deux et trois dimensions.

Dans cette étude, des nanoparticules d'or fonctionnalisées par des dendrimères liquide-cristallins (Au/LCD) ont été préparées avec succès par échange de ligands ou par estérification et, en fonction de la nature et de la proportion des molécules greffées (d'un mésogène G_0 à un dendrimère G_2), elles présentent soit des propriétés mésomorphes soit un comportement d'auto-organisation sur des surfaces à l'échelle nanométrique.

En ce qui concerne la synthèse, trois voies différentes ont été utilisées pour obtenir ces nouveaux matériaux : 1) la synthèse directe de AuNPs en utilisant des dendrimères

thiol par la méthode biphasique de Brust ; 2) l'échange de ligands afin d'introduire des dendrimères thiol ou le groupement OH permettant d'estérifier des dendrimères-COOH ; 3) l'estérification directe de dendrons-COOH sur les Au/pMP.

Chacune de ces approches possède des avantages et des inconvénients. Finalement, c'est l'estérification de dendrons qui s'est révélée être la méthode la plus facile à réaliser et qui nécessite la moindre quantité de dendrimères, un défaut de dendrimères a même permis de n'estérifier qu'une fraction de tous les groupes fonctionnels disponibles. D'autre part, la chromatographie d'exclusion a été utilisée comme une purification efficace dans les premières phases de synthèse de Au/LCDs (pour la synthèse des particules de départ et l'échange de ligands) et l'ultrafiltration s'est révélée être la technique la plus rapide et la plus simple produisant les matériaux finaux fonctionnalisés par les dendrimères avec une très grande pureté.

En ce qui concerne la caractérisation de ces particules, un mésogène chiral G_0 ainsi qu'un dérivé cyanobiphenyl de première génération estérifié sur des Au/pMP ont donné naissance à des mésophases non-caractéristiques. Par ailleurs, les observations TEM ont révélé que le dérivé cyanobiphenyl de première génération a été en mesure de promouvoir l'auto-organisation sur une surface lorsqu'il est utilisé dans une synthèse directe ou dans une réaction d'échange sur l'or, par estérification sur des Au/pMP et dans une réaction d'échange sur des particules d'argent ou de palladium, même si aucune phase liquide-cristalline n'a été observée pour ces composés en utilisant la microscopie à lumière polarisée.

En conclusion, cette étude a mis en avant l'estérification (en plus de la synthèse directe et de l'échange de ligands) comme un moyen efficace pour greffer des dendrimères liquides cristallins sur de petites particules avec une faible polydispersité. Même si seule une organisation de surface promue par les dendrons a été observée à ce jour, une optimisation des paramètres de synthèse des NPs et un remaniement des LCDs pourraient sans doute permettre une meilleure organisation et la possibilité d'accéder à notre objectif : les métamatériaux et leurs remarquables propriétés.

List of abbreviations

Here is a list of the abbreviations used along the manuscript. A schematic representation of nanoparticles and ligands used for the latter is located in appendix 3 as well.

4-mdp	4-(12-mercaptododecyl)phenol
4-ppy	4-pyrrolidinopyridine
AFM	Atomic force microscopy
Ar-R	Aryl-R, R = halide, SH, etc.
AuNPs	Gold Nanoparticles
Col	Columnar phase
Cr	Crystalline or semi-crystalline material
(C ₁₂ H ₂₅ -S) ₂	Dodecyl disulfide
DEN	Dendrimer-encapsulated nanoparticle
dithiolane	4-methylbenzyl 5-(1,2-dithiolan-3-yl)pentanoate
DMAP	<i>N,N</i> -dimethylpyridin-4-amine; 4-(<i>N,N</i> -dimethylamino)pyridine
DPTS	4-(<i>N,N</i> -dimethylamino)pyridinium-4-toluenesulfonate
DSC	Differential scanning calorimetry
C ₁₂ H ₂₅ -SH	Dodecanethiol, <i>n</i> -Dodecyl mercaptan, NDM, Lauryl mercaptan, Mercaptan C ₁₂
C ₆ H ₁₃ -SH	Hexanethiol, mercaptohexane, hexyl mercaptan, Mercaptan C ₆
I	Isotropic
MPC	Monolayer-protected cluster
mud3eg	(11-mercaptoundecyl)triethylene glycol
mud4eg	(11-mercaptoundecyl)tetraethylene glycol

N	Nematic phase
N*	Chiral nematic phase
NCD	Nanoparticle-cored dendrimer
NMR	Nuclear magnetic resonance
PAMAM	Poly(amidoamine)
PEG	Poly(ethylene glycol)
Ph-R	Phenyl-R, R=halide, SH, etc.
pMP	4-mercaptophenol, 4-hydroxythiophenol
POM	Polarizing optical microscopy
PTSA	4-methylbenzenesulfonic acid; <i>p</i> -toluenesulfonic acid
QSE	Quantum size effect
R-SH, C _n -SH	Thioalkane, alkanethiol, mercaptoalkane with a C _n H _{2n+1} alkyl chain
RT	Room temperature
SAXS	Small-angle X-ray scattering
SEC	Size exclusion chromatography
SmA	Smectic A phase
STM	Scanning tunneling microscopy
TEM	Transmission electron microscopy
<i>T_g</i>	Glass transition
TGA	Thermogravimetric analysis
TOAB	Tetraoctylammonium bromide (C ₈) ₄ N ⁺
TPP	Triphenylphosphine (PPh ₃)
UF	Ultrafiltration
UV-Vis	Ultraviolet-Visible spectroscopy

1. Introduction



The Lycurgus Cup in reflected (left) and transmitted light (right). The inclusion of gold (and silver) into the glass is responsible for the green-red dichroism.

Reproduced from the British Museum

1.1. Background

1.1.1. Overview on gold nanoparticles: syntheses and characterization

The Lycurgus cup is probably amongst the first examples of nanotechnology of gold developed in the 4th century AD: it exhibits an outstanding green-red dichroism in reflected and transmitted light (see introduction title page). Roman glass-workers added gold (and silver) when the glass was molten. The reduction of previously dissolved silver and gold, during heat-treatment of the glass, caused the fine dispersion of silver-gold nanoparticles responsible for the color.^[1] Faraday in 1857 described the formation of deep red colloidal solutions of gold by the reduction of gold chloride by phosphorus.^[2] In the last century, in 1951, Turkevich reported the way to obtain gold nanoparticles (AuNPs) in the size range of 10-20 nm by stabilizing them in water by citrate.^[3] But it is 1994 that Brust published a biphasic method that allowed one to obtain 2 nm size particles.^[4] The gold salts are transferred to the organic phase by a quaternary ammonium and are then reduced by a borohydride in the presence of thiols. Brust also extended this synthesis in 1995 to *p*-mercaptophenol-stabilized AuNPs in a single phase.^[5]

For the last fifteen years Brust's method has had a considerable impact on the overall field, because it allowed the facile synthesis of thermally- and air-stable AuNPs of reduced dispersity and controlled size. Since then the large number of publications increased almost exponentially. Thus Astruc published a general review on AuNPs and their applications five years ago.^[6] This goes along with many general publications,^[7-13] reviews^[14-16] and a book^[17] on NPs and their applications.^[18-24]

These particles are named NPs as a general term and clusters when the core is of defined (small) size (the number of atoms composing their core is determined). Besides, they can be viewed as a self-assembled monolayer on flat surfaces (2D-SAMs) transferred to a "spherical" shape defined by a gold core (3D-SAMs).^[25-31] In this case NPs are called monolayer-protected clusters (MPCs).^[32] Furthermore AuNPs are organic-inorganic

hybrids (inorganic gold core and organic thiol ligand shell) that can be easily dispersed in an organic medium which makes them a colloidal suspension. Practically, NPs are improperly but simpler defined as soluble in a given solvent.

AuNPs exhibit a strong absorption band in the visible region which is indeed a particle effect since it is absent from the individual atom as well as in the bulk. This absorption is due to a resonance of the electromagnetic field with the collective oscillation of the conduction band electrons and is known as the surface plasmon resonance (SPR).^[9, 13, 33] In addition, in this size regime AuNPs experience intrinsic size effects: as the size of the particles becomes larger than individual gold atoms the electron energy levels are (quantization) but strongly size-dependent and are known as quantum size effect (QSE).^[9, 34] Finally when particles are large, the energy levels merge into the quasi-continuous band structure as for the bulk solid. The optical and other properties become size-dependent for small AuNPs and can be modulated by controlled synthesis conditions. It is this size dependence that makes nanoparticle-based materials so attractive.

1.1.2. Ligand exchange on gold nanoparticles

The ligand exchange reaction allows one to preserve the size and size dispersion of the initial particles while adding new features. The mechanism was detailed by Murray^[35] and was investigated also by many other groups exchanging thiols for thiols,^[36-42] phosphines for thiols^[43-48] or even dimethylaminopyridine for thiols.^[49]

One of the important aspects of ligand exchange is the morphology of NPs: they present different sites (terraces, edges and vertices),^[35] the reactivity of which is different and depending on the initial ligand, a complete place-exchange becomes impossible. This is the case for thiols.^[41]

1.2. Dendrimer-based AuNPs

1.2.1. Dendrimers and gold nanoparticles

A wide majority of dendrimer/AuNPs combinations are realized by the inclusion of gold into poly(amidoamine) dendrons in aqueous solutions.^[50-61] In this case dendrimers are used as templates, NPs are generally located within the dendritic arms, and are named: dendrimer-encapsulated nanoparticles (DENs),^[52-54] dendrimer-gold nanocomposites,^[50, 56, 58] dendrimer-passivated^[60] or dendrimer protective colloids.^[57] Other dendrimer/AuNPs assemblies were reported: thiol-functionalized Fréchet-type,^[62] Newkome-type,^[63] or poly(propyleneimine) (PPI).^[64]

Another approach which is described in the literature presents a system made of AuNPs as the core and dendrimers as a surrounding stabilizing medium. These hybrids are named dendronized Au colloids,^[65] dendrimer-stabilized AuNPs^[66, 67] or nanoparticles-cored dendrimers (NCDs).^[68, 69] Recently Shon reviewed the strategies used to combine AuNPs and dendrons according to this approach: the esterification of dendrimers on functionalized AuNPs is described.^[70, 71]

1.2.2. Liquid-crystalline dendrimers and gold nanoparticles

The combination of liquid-crystals (LC) and AuNPs was mainly reported as physical mixture of the two. Hegmann published recently a review on that topic.^[72] He as well as many other groups actively participate in the field: some of the mixtures are obtained with lyotropic LCs^[73-75] and the others with thermotropic ones.^[76-91] In particular, such systems enhanced the electrical properties of the resulting material.^[79, 85, 87]

Another approach consists in anchoring the LC moiety directly to the Au core; the resulting entity can be combined with LC of the same type or considered as an independent system.^[92-94] This was made possible by the synthesis of tailored ligands generally bearing a thiol function.^[92, 93, 95-99]

However only a few of these systems are dendritic^[100-103] and the main studies in the LC-tethered AuNPs field concerns mesogenic ligands.^[80, 90, 93, 95-98, 100, 104-106]

1.2.3. Self-assembly of dendrimer-containing gold nanoparticles

Particles are capable to self-assemble and this organization of NPs is driven by wetting and by different forces such as capillary, dispersion or van der Waals forces.^[107-109] Sometimes a temperature gradient creates instabilities when the sample containing particles is deposited on a surface; consequently ring-shaped structures are observed.^[110, 111]

Under favorable conditions self-assembly of particles in 2D^[112-114] or even 3D^[97, 108, 109, 115-117] can be observed. Organization of particles can also be achieved by block copolymer.^[118-122]

Furthermore, this organization can lead to improved optical and electrical properties.^[79, 85, 87, 123] And even a special category of material can be obtained by the 3D assembly of small nanoparticles covered by dendrimers.^[124, 125] These materials can exhibit a negative index of refraction and are called metamaterials.^[126-137]

1.2.4. Motivation of thesis

It has been shown by calculations that metamaterials with effective negative index of refraction can be obtained by organization of metal nanoparticles.^[124, 125] The basic idea of this thesis is to use liquid-crystalline dendrimers attached to metal nanoparticles as a vehicle to organize the latter. Therefore the goal of the thesis was the preparation of small, mono-disperse metal nanoparticles and the development of a strategy to covalently bind liquid-crystalline dendrimers. Finally, it should be tested if these new composite materials self-assemble in two and three dimensions.

1.3. Outline

The first chapter of this manuscript deals with the direct synthesis of AuNPs and the ligand exchange reaction to add functional groups into the shell of non-functional AuNPs. Selected illustrative examples of the scientific literature are detailed to understand the stakes of such reactions with AuNPs. Several points will be developed including the size

control, the structure, purifications and characterization within Brust's method. As far as ligand exchange is concerned, the mechanism, the ability to introduce new functionalities and the purifications subsequent to exchange will be detailed. At last results will be presented showing the choices which were made in terms of direct synthesis and ligand exchange required for the particles used in the subsequent reactions.

The second chapter will describe the functionalization of AuNPs with dendrimers. First the relation between AuNPs and dendrimers will be illustrated with some examples from the literature. Then the adopted strategy consisting in the esterification of dendrons onto AuNPs will be detailed and some examples given. The following section will detail the combination of AuNPs and liquid-crystalline (LC) dendrimers, first as a mixture and secondly when the LC dendrimers are tethered to gold. Finally the results of the attempts in coupling AuNPs and LC-crystalline dendrimers will be reported for both the direct synthesis and the ligand exchange. The purification of such compounds will be discussed at the end.

The third chapter will address the assembly of LC-dendrimer-based AuNPs. First it will be the phenomenon of self-assembly that will be described as well as all the forces involved in this phenomenon. Then we will discuss about the two-dimensional and three-dimensional assembly and give some examples of block-copolymer-mediated assembly. After that it will be the potential optical properties that will be presented and finally the assembly of particles synthesized as described in the previous chapter.

In addition the manuscript includes appendices. The first one brings generalities and details on the size exclusion chromatography and ultrafiltration used to purify AuNPs. The second appendix gives the characteristics of the dendrons used as well as of on the synthesized particles. Appendix three explains the formalism adopted in the manuscript and depicts all ligands and NPs of this thesis. Finally, Appendix four gives details on the calculations used to characterize the AuNPs.

Forewords

With the aim of alleviate the notations concerning AuNPs, a formalism was adopted (details in the Third appendix). Briefly, nanoparticles will be referred to as “Au/” followed by the name of the ligand – or ligands in the case of a mixture and they will be separated by a vertical bar “|”. The exchange of ligands will be denoted as the plus-minus sign “±” and finally the esterification will be symbolized by the right curly bracket “}”. For example: AuNPs stabilized by ligand A subsequently exchanged by ligand B on which dendron C is esterified will be noted: Au/A±B}C.

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2. Syntheses and ligand exchange

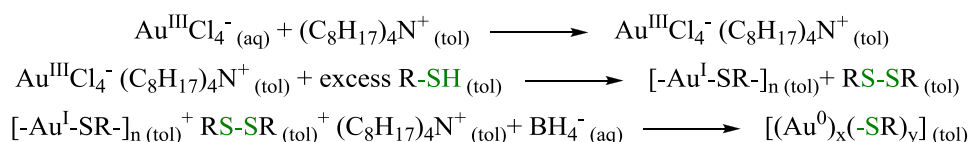
Michael Faraday about "[...] gold: it is clear that that metal, reduced to small dimensions by mere mechanical means, can appear of two colours by transmitted light, whatever the cause of the difference may be. The occurrence of these two states may prepare one's mind for the other differences with respect to colour, and the action of the metallic particles on light, which have yet to be described."

*M. Faraday, The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light. Phil. Trans. R. Soc. **1857**, 147, 145-181*

2.1. Brust's synthesis adapted

2.1.1. Size control over growth of gold nanoparticle cores

Brust and co-workers introduced a two-phase method to obtain gold nanoparticles involving the transfer of a gold salt, HAuCl_4 , from the aqueous phase to the organic one thanks to a phase-transfer agent (tetraoctylammonium bromide, $(\text{C}_8\text{H}_{17})_4\text{N}^+$). Then the gold salt is reduced by borohydride salt (NaBH_4) in the presence of an alkanethiol (dodecanethiol) according to **Scheme 1**. Rather small particles in the range of 1–3 nm are obtained in this way, unusually stable for thiol-derivatized metal nanoparticles that can be handled and characterized like simple chemical compounds.^[1] Preparation of colloidal metals was already described by Michael Faraday in a two-phase system – aqueous gold salts and phosphorus in carbon disulfide – producing particles with average sizes in the 6 ± 2 nm range.^[2, 3]



Scheme 1 – The two-step procedure introduced by Brust:^[1] the gold salts are transferred to the organic part then reduced by an excess of thiols to a gold(I)-thiolate polymer and finally Au(0) NPs are formed by borohydride reduction. Note that in the end AuNPs are accompanied of thiols, disulfide, $(\text{C}_8\text{H}_{17})_4\text{N}^+$ and chlorides as remaining impurities.

The implementation of Brust's technique was immediately followed by refinements of the technique: the gold-to-thiol ratio can control thermodynamically the size of gold nanocrystals.^[4] In 2000, Hutchison and co-workers described a more versatile and convenient synthesis of phosphine-stabilized gold nanoparticles (AuNPs) giving rise to 1.5 ± 0.4 nm particles:^[5] a combination of Brust's technique and Schmid's phosphine-stabilized AuNPs.^[6] The latter avoids the cumbersome rigorously anaerobic conditions and the use of diborane as reducing agent.^[6] Indeed phosphine-stabilized AuNPs are

excellent precursors for other functionalized nanoparticle building blocks possessing well-defined metallic cores.^[7]

A seeding growth approach was described by Murphy and co-workers where AuNPs with any diameter from 5 up to 40 nm with 10-15% standard deviation can be prepared starting from 3.5 nm AuNP seeds by varying the ratio of seed to metal salt.^[8]

Another important point influencing the size of AuNP is the nature of the stabilizing agent. Phosphanes and thiols turned out to be excellent stabilizers due to the rather strong Au–P bonds or even stronger Au–S bonds. These molecules allow the isolation of AuNPs as solid materials that can be redispersed in appropriate solvents. This is not possible with weakly binding stabilizers such as citrate.^[9] Using mercaptosuccinic acid and by varying the ratio allowed Chen and Kimura to access 1–3 nm water-redispersable NPs.^[10] 11-mercaptoundecanoic acid was also used as a protecting agent to have functional groups for further attachment to a silica film.^[11] Also mixed monolayers of ligands can stabilize AuNPs, for example one with an alkane chain and the other with an –OH group at the tail of the alkane chain. It was found that many parameters do influence the resulting NP size: adsorption of polar components is largely favored because of the poorer solvation of polar tail groups in toluene compared to THF where the tail group effect is much less pronounced. In more polar solvents such as THF, a large thermodynamic control promotes a preferential adsorption of the thiols with a longer alkyl chain onto the NP surface. It appears that AuNPs generated in polar solvents are smaller than the ones grown in apolar solvents in the same conditions.^[12]

One can control the core size and composition through careful choice of reaction conditions during synthesis or by post-synthetic modifications such as Ostwald ripening and size-selective purification (e.g. fractional crystallization, gel electrophoresis^[13, 14]). Despite these advances, precise control over the core size and size dispersity remains a challenge.

The advantages of all of these methods are (i) good control over the particle size and dispersity by tuning the gold salt-to-ligand ratio and reaction conditions,^[15] (ii) the possibility of introducing a variety of functionalized ligands, and (iii) simple isolation, cleaning, and redispersion of the particles in different solvents. Disadvantages are the impurities that are introduced by the use of surfactants and the restriction of carrying out the reduction in the presence of the capping ligand. The latter can be partially

circumvented if functional ligands are introduced by ligand exchange reactions on stable nanoparticles.^[16, 17] However, this approach is generally more elaborate and still suffers some limitations, especially the problem of getting a complete ligand exchange.

AuNPs can also be synthesized from a solution of tetrachloroaurate in diethylene glycol dimethyl ether (diglyme) and further reduction by a solution of sodium naphthalene in diglyme.^[18] According to this technique, stabilizing surfactant is not required and the resulting weakly protected nanoparticles can straightforwardly be stabilized and functionalized by the addition of a variety of ligands.

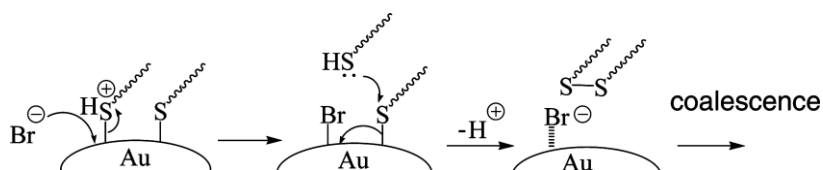


Figure 1 – Schematic illustration of speculated acid-assisted and bromide anion-assisted coalescence mechanism of dodecanethiol-protected AuNPs. Taken from Teranishi.^[19]

Teranishi *et al.* showed that even in the absence of air, coalescence of AuNPs is observed due to the presence of bromide and proton acid leading to the formation of dodecyl disulfide ((C₁₂H₂₅-S)₂) from the removal of dodecanethiol (C₁₂H₂₅-SH) which was probed by ¹H NMR (see **Figure 1** for schematic illustration). (C₁₂H₂₅-S)₂ oxidation is not due to the presence of oxygen because the sample was strictly freeze-evacuated, N₂-substituted and sealed, and moreover C₁₂H₂₅-SH is not oxidized when AuNPs are not present.^[19]

Murray *et al.* reported an extended study on the various conditions influencing the particle core in dodecanethiol-capped AuNPs (Au/C₁₂H₂₅-SH).^[15] It was showed that as more thiol is added (decreasing the Au/thiol ratio), the NPs become smaller.^[4, 15] Using a ratio less than 10:1 for reductant to gold yields aggregates. Alternative reductants to borohydride such as superhydride,^[20, 21] amine^[22] or amine-borane^[23] lead generally to bigger particles. A faster delivery of the reductant gives birth to smaller particles with lower dispersity.^[15, 24] The temperature at which the reaction occurs has an influence on the size dispersity with larger dispersity at higher temperature – Jørgensen *et al.* showed a linear relation between the average size of the clusters and their preparation temperature.^[25] Indeed, the formation is controlled by kinetic competition, which can also explain the higher polydispersity at elevated temperature.

2.1.2. Structure of small thiolate-protected gold nanoparticles

DFT calculations showed that thiolate-protected gold nanoclusters, namely $\text{Au}_{38}(\text{SCH}_3)_{24}$, exhibit a novel structural motif consisting of ring-like $(\text{AuSCH}_3)_4$ units protecting a central Au_{14} core.^[26] It was later confirmed by Jadzinski *et al.* by determining the structure of $\text{Au}_{102}(\textit{p}\text{-mercaptobenzoic acid})_{44}$ using X-ray crystallography.^[27] Indeed they found that it is composed of a gold core surrounded by staple motifs consisting of thiolates and gold atoms that are somewhat detached from the dense gold core (see **Figure 2-C**).

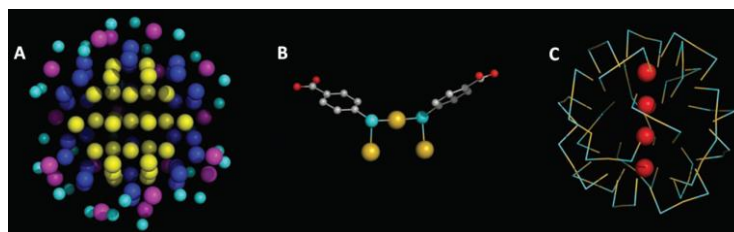


Figure 2 – Sulfur-gold interactions in the surface of the nanoparticle. (A) Successive shells of gold atoms interacting with zero (yellow), one (blue), or two (magenta) sulfur atoms. Sulfur atoms are cyan. (B) Example of two *p*-mercaptobenzoic acids (*p*-MBAs) interacting with three gold atoms in a bridge conformation, here termed a staple motif. Gold atoms are yellow, sulfur atoms are cyan, oxygen atoms are red, and carbon atoms are gray. (C) Distribution of staple motifs in the surface of the nanoparticle. Staple motifs are depicted symbolically, with gold in yellow and sulfur in cyan. Only the gold atoms on the axis of the Marks decahedron are shown (in red). Taken from Jadzinski *et al.*^[27]

Whetten *et al.* recently established a parallel between $\text{Au}_{144}(\text{SR})_{60}$ and $\text{Au}_{114}(\text{RS-Au-SR})_{30}$ by comparing X-ray scattering structure factor – for 29 kDa thiolate-protected cluster – and DFT computations. They found that there was an excellent fit of the structure factor to the experimental measurements.^[28] Moreover it allows one to consider that $\text{Au}_{144}(\text{SR})_{60}$ cluster may serve as an important intermediate-size system for investigations on how the gold-sulfur nanointerface evolves from small particles with a high-curvature Au/S interface to that of the zero-curvature Au(111)/SAM bulk interface.^[29]

$\text{Au}_{144}(\text{SR})_{60}$ was analyzed in terms of the “superatom-complex model” (SACM), elucidated for thiolate-protected clusters revealing that $\text{Au}_{144}(\text{SR})_{60}$ accounts for the reported optical and electrochemical properties of the 29 kDa nanoparticle. According to SACM, $\text{Au}_{144}(\text{SR})_{60}$ has $144 - 60 = 84$ “metallic” electrons in the neutral state, meaning that it is deficient by 8 electrons from the shell closing of 92 electrons.^[30]

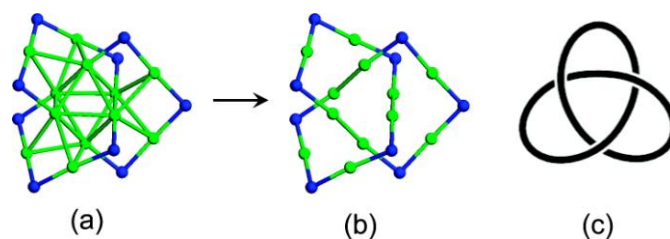


Figure 3 – The Au_{12}S_9 framework (a) of $\text{Au}_{12}(\text{SR})_9^+$ is related to the trefoil knot (c) by viewing the connections in the framework as in part b. Au, green; S, blue; C and H, not shown. Taken from Jiang *et al.*^[31]

Structure-bonding considerations lead Whetten *et al.* to propose $\text{Au}_{12}(\text{SR})_9^+$ as a candidate for the smallest thiolated gold superatom as an octahedron core covered by three $\text{RS}(\text{AuSR})_2$ motifs with a unique C_3 axis. This structure is chiral and possesses aurophilic interactions (see **Figure 3**).^[31]

2.1.3. Purifications at issue

Concerning the purification of the particles synthesized by the Brust's two-phase technique, AuNPs have to be separated from three excess reagents: the ammonium salts from the phase-transfer, borohydride salts from the reduction and finally the excess thiol ligand required in this synthesis (see **Scheme 1**).

Purification is one of the major issues in nanoparticle syntheses. Moreover some metallic particles are sensitive to air and moisture and as a consequence handling is more difficult. In general AuNPs are not very sensitive to air and moisture which give the opportunity to use various purification methods. Many of them were investigated in order to find the more convenient ones to easily and rapidly access purified particles such as column chromatography, electrophoresis, size exclusion chromatography, membrane filtration, ultrafiltration under N_2 pressure, centrifugation, ultrafiltration by centrifugation, fractional precipitation. Other interesting methods exist but were not tested because of setup or time issues: diafiltration based on tangential flow filtration^[32] and Soxhlet extraction.^[33]

One of the first conclusions is that the purification highly depends on the nature of the particles (polarity of the protecting shell), their size as well as on the compounds to be separated from the particles (transfer agent, free alkane thiol ligand and end-functionalized analogues, dendritic ligands bearing a thiol function or not). Some of these techniques works for the starting materials involving one particular alkane thiol ligand

(e.g. membrane filtration for Brust particles) but are totally ineffective when different types of ligands are in the particle shell (e.g. membrane filtration in the case of a mixed monolayer of alkane thiol ligands and dendritic ligands bearing a thiol function in the shell of particles).

A purification method was proposed by Schiffrin and co-workers to separate AuNPs from the quaternary ammonium salt (TOAB)^[33] – used as the phase transfer reagent in the original Brust-Schiffrin two-phase synthesis:^[1] it consists in a 12 h-period Soxhlet extraction in toluene.

Hutchison and co-workers described the use of diafiltration (see **Figure 4** for schematic representation) for the purification and separation of polydisperse samples of AuNPs.^[32]

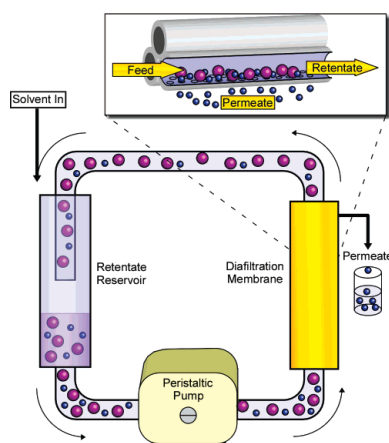


Figure 4 – Schematic representation of the continuous diafiltration setup used by Hutchison *et al.*^[32]

In our case it was found that washing cycles followed by redissolution were the most efficient way to obtain highly purified particles from both TOAB and free thiol ligands. Nevertheless, the original precipitation with ethanol in toluene^[1] was replaced by filtration over regenerated-cellulose (RC) membranes (pore size is 0.2 μm , and nylon-based membranes working as well as the RC ones) after alternatively washing with equivalent volumes of alcohol and acetone (five times 100 mL of each) the particles are finally redissolved with the help of n-heptane (less volatile than shorter chain n-hexane or n-pentane) leaving the ionic phase-transfer agent and aggregated material over the membrane. The washing cycle was repeated at least twice or until no trace of free thiol was detected by TLC.

It was also shown that alkane thiol-capped gold nanoparticles can be dissolved in supercritical ethane in which the solubility was found to be dependent on the core diameter thus allowing size-separation.^[34]

2.1.4. Characterization

AuNPs stabilized by chemisorbed monolayers of alkanethiolate can be investigated in solution and in the solid phase. These materials can be dried free of solvent to form a dark brown solid that can be re-dissolved in non-polar solvents. Their exceptional stability suggests that they can be viewed as *cluster compounds* or *macromolecules*. The self-assembled alkanethiolate monolayers stabilizing the metal nanoparticles can be investigated using techniques that are insufficiently sensitive to study a monolayer on a flat surface, e.g., ^1H and ^{13}C NMR, elemental analysis, differential scanning calorimetry (DSC), and thermogravimetry (TGA). Results from such measurements, combined with small-angle X-ray scattering (SAXS) data of solutions of the clusters and images from scanning tunneling (STM), atomic force microscopy (AFM) and transmission electron microscopy (TEM), giving information on structure, size, shape and composition of the AuNPs.

2.1.4.1. NMR

Murray *et al.* reported that high-resolution NMR spectra of cluster solutions display well-defined resonances except for the methylene groups the nearest to the gold interface.^[35] It is well known that NMR line broadening for proteins and polymers is dominated by their slow rotation in solution; the alkanethiolate-protected clusters are analogous, slowly rotating macromolecules. Multiple factors appear to contribute to the signal broadening:^[15] (a) the methylenes the closest to the thiolate/Au interface are the most densely packed and solid like, and thereby experience fast spin relaxation from dipolar interactions. The methylenes far away from the Au core experience freedom of motion and spin relaxations more similar to those of dissolved species.^[35, 36] This broadening effect thus rests on the structural features of the monolayer. (b) The distribution of chemical shifts caused by differences in the Au-SR binding site (terraces, edges, vertices, see **Figure 11**) was proposed to be responsible for the substantial broadening of the ^{13}C resonance for the R- and $\alpha\text{-CH}_2$ groups in a solid-state AuNP sample.^[36] This effect falls off sharply with distance from the metal core. (c) Spin-spin relaxation (T_2) broadening

depends on the rate of rotation of the cluster molecules in solution, and for the methyl resonance it should vary as r^{-3} ,^[15] where r is the average methyl-to-Au core center distance. Murray observed that the width of methyl group resonances varies systematically with core size and presented the evidence for the quantitative importance of T_2 broadening for the Au cluster NMR resonances in solutions. And however, practically, it was observed that the atoms the farthest away from the NP surface display broadened signals even for second generation dendrons (see 3.4.2).^[37-39]

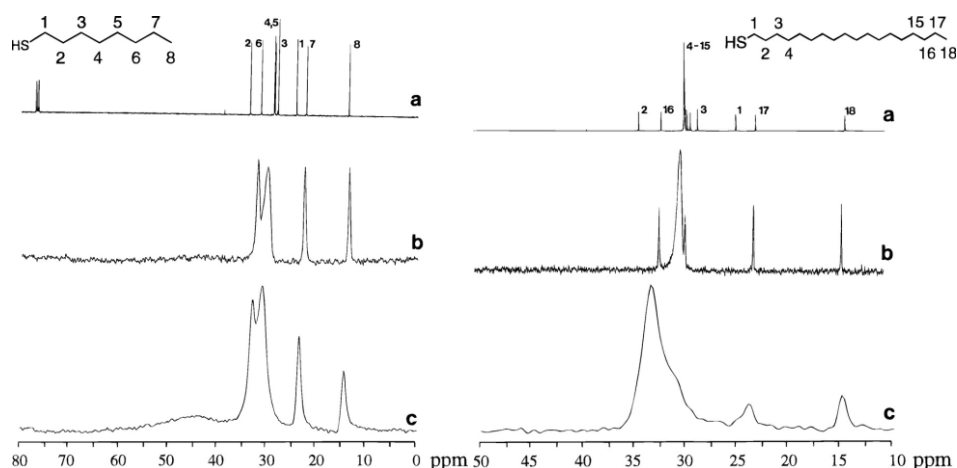


Figure 5 – ^{13}C NMR spectra of octanethiol (left) and octadecanethiol (right): (a) as a free ligand, (b) on colloidal gold in benzene- d_6 , and (c) on colloidal gold in the solid state. Taken from Badia *et al.*^[36]

Reven reported solid-state ^{13}C NMR studies of short and long chains alkanethiols adsorbed on AuNPs at variable temperatures.^[36] In both the solution and solid state, the resonances of the first three carbons next to the sulfur headgroup disappear upon binding to the gold, indicating a strong interaction with the surface (see **Figure 5**).

Reven *et al.* also reported that the chemisorbed species on the gold nanoparticle surface is most probably a thiolate, not a disulfide, given the similarity in the ^{13}C chemical shifts of the Au/SR colloids and Au(I) alkylthiolates. The interactions responsible for the line broadening of the C1 and C2 sites are consistent with the particles being faceted. No evidence for a Knight shift contribution to the C1 shift is observed. The excellent correspondence observed thus far, between the properties of thiols absorbed on planar and colloid surfaces, indicates that conclusions based on ^{13}C NMR studies of gold-sulfur interactions in the nanoparticle system are transferable to the planar RS/Au SAMs.^[40]

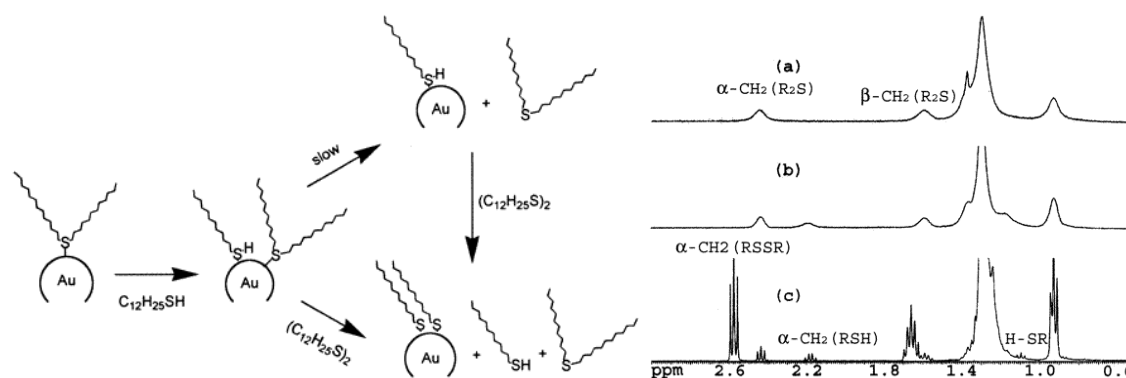


Figure 6 – On the left: Reaction scheme of ligand addition and replacement reactions on the cluster surface. On the right: ¹H NMR spectra of (a) dodecyl sulfide-capped gold clusters in perdeuterated benzene, (b) clusters after addition and uptake of 2 molar equiv of dodecanethiol with respect to thioether in the ligand shell, and (c) after ligand shell replacement and release of free dodecanethiol (α-methylene quartet centered at 2.18 and S–H triplet at 1.10 ppm) and dodecyl sulfide (α-methylene triplet at 2.44 ppm) following addition of excess dodecyl disulfide (α-methylene triplet at 2.58 ppm). Both taken from Hasan *et al.*^[41]

Brust *et al.* have shown experimentally that thiol–gold systems in which *intact* thiols are still present can be prepared under certain conditions and are easily characterized by ¹H NMR spectroscopy.^[41] It is demonstrated that thiols can adsorb to gold without losing hydrogen. Dodecyl sulfide-capped gold clusters have been prepared and subjected to ligand exchange reactions in perdeuterated benzene by addition of dodecanethiol and subsequently dodecyl disulfide. It is shown by ¹H NMR spectroscopy that dodecanethiol molecules are readily taken up as ligands producing characteristic broad signals corresponding to the α-methylene and S–H protons, with chemical shifts close to those found for thiol in solution; these signals are absent in spectra of thiolate-capped clusters. Addition of excess disulfide to such clusters capped with both dialkyl sulfides and thiols leads to the appearance of sharp signals for free dialkyl sulfide and *intact* thiol. Amounts of thiols up to 50% of the ligand shell are, however, taken up by the clusters under rapid and irreversible loss of hydrogen (illustrative scheme and NMR spectra are shown in **Figure 6**).

Tong *et al.* reported observations of particle-size effect on NMR observables of the most proximal carbon to the Au surface, C1. It demonstrates that the ¹³C NMR of the protecting, C1-labeled octanethiol (or alkanethiol in general) is indeed a sensitive function of the underlying particle size, therefore, is promising to be used as a powerful microscopic probe to investigate in detail the effect of the quantum confinement and the metal–ligand interaction.^[42]

Triphenylphosphine-capped, 1.5-nm gold nanoparticles “Au₁₀₁(PPh₃)₂₁Cl₅” prepared following Hutchison’s procedure^[5] undergo rapid exchange of capping ligand phosphine with dissociated and added phosphine in dichloromethane solvent at 298 K. Remarkably, while the ¹H NMR spectrum resonances of the attached phosphine are broad, characteristic of a range of incompletely averaged environments, the ³¹P NMR spectrum (observable only at 213 K and below) exhibits a single, narrow resonance indicating that all of the phosphorus atoms are magnetically equivalent.^[43]

In contrast to the proton NMR spectrum of Au₁₀₁ exhibiting very broad peaks as have been observed for alkanethiolates bound to gold nanoparticles, these broad signals have been attributed to the heterogeneity of sites presented by the nanoparticle surface and to the slow rotation (as for proteins and other macromolecules) in solution. Consistent with the latter dependence on *T*₂, line width was found to increase with particle size.^[15]

In striking contrast to the range of capping ligand environments indicated by the ¹H NMR spectra, the Au₁₁, Au₅₅, and Au₁₀₁ clusters each exhibit a single phosphine resonance, despite the fact that PPh₃ must be bound to chemically inequivalent sites in all three clusters. Discussed by Schmid for the larger clusters,^[44] rapid motion of the phosphine along the particle surface was invoked. In the case of the small clusters, no evidence of such dynamic behavior was found, although facile, fluxional motions of the metal skeleton have been considered as a source of the phenomenon. In mixed PPh₃, PR₃ clusters, the ³¹P-³¹P coupling through the gold cluster was considered to provide the mechanism for inducing magnetic equivalence of the different sites. Evidently, the gold cluster core provides a mechanism for producing magnetic equivalence of the phosphorus atoms in these clusters.^[43]

Ligand exchange reactions were monitored by fluorescence provided that a fluorophore label is present on gold nanoparticles. Todd Emrick and co-workers^[45] not only followed place exchange reaction by NMR but also by fluorescence because thiolated boron-dipyrromethene (Bodipy) dye was added to particles by ligand exchange on pentanethiol protected gold nanoparticles. They used primary, secondary and tertiary thiols and demonstrated that primary thiols are more active than the corresponding secondary or tertiary thiols thus showing that steric hindrance near the thiol group significantly reduces the reactivity in place exchange reactions.

Murray *et al.* described the effects of oxidative electronic charging of the Au cores of MPCs on NMR spectra of their monolayer ligand shells. Previously unresolved fine structure in the ^{13}C NMR hexanethiolate methyl and C5 methylene resonances is seen in spectra of solutions of monodisperse Au_{140} MPCs, reflecting magnetically inequivalent ligand sites. Incremented electrochemical increases in positive cluster core charge cause the spectral fine structure of the methyl resonance to coalesce, becoming a single peak at the Au_{140}^{3+} charge state. The spectral changes are reversible; charging back to the original core charge state regenerates the methyl ^{13}C resonance fine structure. Adding an equimolar quantity of a Au(I) thiolate complex, to an uncharged Au_{140} MPC solution in d_2 -methylene chloride causes partial spectral coalescence. ^{13}C NMR spectra of Au_{38} MPCs exhibit roughly comparable spectral changes upon positive core charging to the '0', '+1', and '+2' states. The NMR results indicate that exchange between magnetically inequivalent sites occurs at rates of 100 to 400 s^{-1} , rates believed to be accountable by actual exchanges of ligands between different sites on the Au core.^[46]

2.1.4.2. UV-Vis

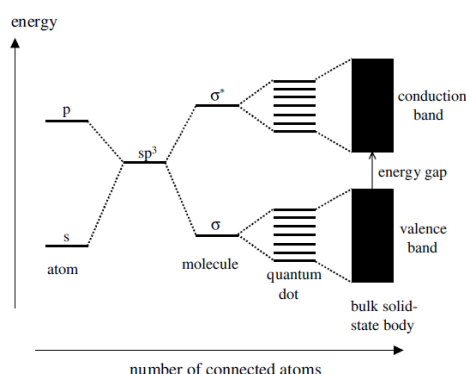


Figure 7 – Electronic energy levels depending on the number of bound atoms. By binding more and more atoms together, the discrete energy levels of the atomic orbitals merge into energy bands (here shown for a semi conducting material). Therefore semiconducting nanocrystals (quantum dots) can be regarded as a hybrid between small molecules and bulk material. Taken from Schmid.^[47]

Being at the nanometer length scale, $\text{Au}_n(\text{SR})_m$ nanoparticles are in the quantum size regime^[48, 49] (quantum size effect, QSE) where the continuous electron bands of bulk Au become discrete (see **Figure 7**). In this size regime, certain properties of the noble metal nanoclusters, such as the conduction electron plasmon resonance (surface plasmon band, SP band), begin to scale in a predictable fashion with size and state of aggregation of the nanoclusters. The plasmon resonance of gold and silver are also sensitive to the

surrounding environment, which enables a plasmon resonance spectroscopy of the nanoclusters that is sensitive to the nature of the capping group and dispersing medium.^[50-52] This size dependence can cause these capped metal nanoclusters to be conducting, semiconducting and even insulating as the nanocluster size is decreased.^[53] Experimentally, small AuNPs exhibit a strong UV absorption feature which decays approximately exponentially into the visible, with a superimposed broad band at about 520 nm that decreases in intensity and energy with decreasing AuNP size.^[15]

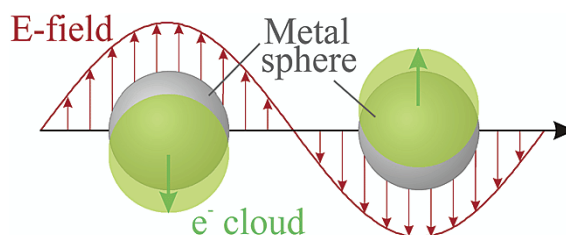


Figure 8 - Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei. Taken from Schatz.^[54]

When a small spherical metallic nanoparticle is irradiated by light, the oscillating electric field causes the conduction electrons to oscillate coherently.^[54] This is schematically pictured by Schatz in **Figure 8**. When the electron cloud is displaced relative to the nuclei, a restoring force arises from Coulomb attraction between electrons and nuclei that results in oscillation of the electron cloud relative to the nuclear framework. The oscillation frequency is determined by four factors: the density of electrons, the effective electron mass, and the shape and size of the charge distribution. The collective oscillation of the electrons is called the dipole plasmon resonance of the particle (sometimes denoted “dipole particle plasmon resonance” to distinguish from plasmon excitation that can occur in bulk metal or metal surfaces). For a metal like silver, the plasmon frequency is also influenced by other electrons such as those in d-orbitals, and this prevents the plasmon frequency from being easily calculated using electronic structure calculations.

Rothenberg presented a new method for estimating the size of nanoclusters from UV-visible spectroscopy and Mie theory.^[52] The core/shell approach enables the estimation of metal cluster sizes directly from the UV-visible spectra, even for transition metal nanoclusters such as Pd that have no distinct surface-plasmon peak in the UV-visible region. Thus they estimated the Pd core size and the Au shell thickness directly from UV-visible spectra. The results of the simulations and fast UV-visible spectroscopy

experiments were validated by transmission electron microscopy which remains the most accurate.

sample	from TEM images			MG fitting					
	radius (nm)	standard deviation	Abs @ SPA _{MAX}	R (nm)	ΔR	Spheres %	S_G	σ_{ext} @ SPA _{MAX} (m ⁻²)	AuNP Conc. (M)
AuNP-1	7.0	61%	0.131	7.4	+6%	77.0%	1.75	1.1 E-16	2.2 E-9
AuNP-2	4.2	28%	0.099	3.8	-10%	97.5%	1.25	1.2 E-17	1.6 E-8
AuNP-3	5.0	42%	0.090	5.1	+2%	94.0%	2.85	3.2 E-17	5.4 E-9
AuNP-4	2.2	22%	0.043	2.2	0%	94.0%	1.75	1.9 E-18	4.3 E-8
AuNP-5	8.9	64%	0.233	8.9	0%	76.0%	1.30	2.2 E-16	2.0 E-9

Table 1 – Mie-Gans fitting results for AuNP solutions in water. We can notice that the difference between experimental and calculated radii ΔR is below 10 %. Abs and σ_{ext} @ SPA_{MAX} are respectively the absorbance and the molar absorptivity corresponding to the wavelength of the surface plasmon band, S_G is the standard deviation of length/width ratio. Taken from Amendola *et al.* [55]

Meneghetti reported a method for the evaluation of the average size of gold nanoparticles based on the fitting of their UV-Vis spectra by the Mie model for spheres. The method gives good results using a calibration of the dumping frequency of the surface plasmon resonance and accounting for the presence of non-spherical AuNP in solution by the Gans model for spheroids. It was applied to free and functionalized gold nanoparticles with diameters in the 4-25 nm range in various solvents. Despite the differences among samples, they found an accuracy of about 6% on the nanoparticles average size (**Table 1**) with respect to sizes measured by transmission electron microscopy (TEM). Moreover, the fitting model provides other information not available from TEM like the concentration of AuNP in the sample and the fraction of non-spherical nanoparticles, which is particularly useful for measuring aggregation processes. [55]

2.1.4.3. Transmission electron microscopy

Transmission electron microscope (TEM) has been a potent tool in earlier investigations of the size and shapes of alkanethiolate-capped AuNPs. [56] TEM is a versatile tool that provides not only a real space image of the atom distribution in the nanocrystal and of its surface, but also chemical information at a spatial resolution of 1 nm or better allowing direct identification of the chemistry at a nanocrystal. For example, TEM in the Brust *et al.* report [1] led to an early estimate that the typical shape was either icosahedral or cuboctahedral; Murray *et al.* reported a truncated octahedral shape for Au clusters from a diameter of 1.3 to 5.6 nm, except for the 2.2-nm AuNP that exhibited a cuboctahedron shape. [15] The contrast is given by the electron density for this technique. Since the

electron density is much higher for the gold core, the thiol layer will not directly be observed.

TEM is almost always the first method used to determine the size and size distribution of nanoparticle samples. Once a representative group of images is obtained, the next task is to count as many particles as possible, ideally a few thousand, so that a representative sample of the size and size distribution can be obtained. To avoid the “by eye and by hand” method, tedious and unrepresentative of the whole sample, a computer-assisted method is preferable. Woehrle *et al.* reported on the use of such softwares^[57] to have a fast and reliable count of nanoparticles to access the mean size and size distribution. A subsequent calculation allows one to estimate the number of core as well as surface atoms, assuming a spherical shape and the density of AuNPs being equal to that of bulk gold for this approximation^[25, 35] (details are given in the Fourth appendix).

Representative TEM observation images are reported in the chapter entitled *Assembly of Dendrimer-containing Gold Nanoparticles* (see 4.3).

2.1.4.4. Thermogravimetric analysis

Murray *et al.* have shown that thermogravimetric analyses (TGA) yielded an organic weight fraction for the clusters that is consistent with their elemental analyses.^[35] They also noted that mass spectra results show that the material thermally desorbed is predominantly the corresponding disulfide and does not contain Au;^[15] visual inspection shows that the material remaining after thermolysis is essentially pure Au. Qualitatively, one expects that the weight fraction of alkanethiolate in the clusters should parallel the cluster core size, and this expectation is realized in the experimental results provided by Murray.^[15]

On a very large cluster, the calculated coverage percentage ($100 \times$ thiolate per surface Au atom) approaches that of a flat Au(111) surface (i.e., 33%, see Whitesides for details).^[58] An analysis of results based on a Au₃₀₉ cuboctahedral cluster gave a 66% coverage, reflecting the combination of a large proportion of edge and vertex atoms on these nanoparticles and their high radius of curvature; indeed a sphere of this diameter covered by tightly packed alkanethiolates ligands can achieve a maximum coverage of 43 % and thus the presence of faces, edges and vertices significantly increases the ligand density of a polyhedron of the same average diameter.^[15]

The relationship between the core size and the TGA organic percentage can be analyzed by two methods: a first one using TEM experimental core size determinations along with experimental TGA results to estimate an experimental coverage percentage; in a second one, the surface areas of ideal polyhedra are divided by the surface area footprint of an alkanethiolate ligand (0.214 nm^2)^[59] which gives for each polyhedron the number of alkanethiolate chains, a calculated TGA organic and coverage percentages (assuming that the polydispersity of the sample could bias the result of the calculation). However the calculated TGA figures are maximal for each polyhedron because a sterically limiting fit of ligands on each surface is presumed.

On the one hand the calculated values (2nd method) are consistent with the experimental observations and on the other hand these latter are in a good match with the experimental coverage determination (1st method).^[15] As a consequence the first method is used as the main way to estimate the coverage percentage of AuNPs.

2.1.4.5. Complementary techniques

Even though the most common characterization technique is high-resolution transmission electron microscopy (HRTEM), which gives a photograph of the gold core of the AuNPs,^[60] the core dimensions can also be determined using scanning tunneling microscopy (STM),^[35, 61, 62] scanning electron transmission microscopy (STEM),^[63] atomic force microscopy (AFM),^[64-68] small-angle X-ray scattering (SAXS),^[35, 69-73] laser desorption–ionization mass spectrometry (LDI-MS),^[74, 75] and X-ray diffraction.^[4] The mean diameter, d , of the cores allows an estimation of the mean number of gold atoms N_{Au} in the cores by calculations^[4, 25, 35] (see also Fourth appendix). From these data, the elemental analysis, giving the Au/S ratio, allows calculation of the average number of S ligands. This number can also be deduced from X-ray photoelectron spectroscopy (XPS) or thermogravimetric analysis (TGA).^[75]

Astruc and Schmid's reviews on AuNPs and references therein provide an exhaustive list of characterization techniques as well as detailed examples.^[60, 76]

2.2. Ligand exchange

Ligand exchange reaction is a simple and versatile approach applicable to a wide variety of ligands and, importantly, maintains the small core size and narrow dispersity of their precursor particles.^[77] With this method, the size, functionality, and physical properties of the ligand shell surrounding the gold nanocrystals can be tuned.^[78]

2.2.1. Exchange of stabilizing ligands

Ligand exchange reaction on gold nanoparticles has proven to be a facile process to yield thiol-stabilized gold clusters starting from phosphine-stabilized AuNPs.^[78]

Silsesquioxanes derivatives were also used in replacement of phosphine stabilizers on gold leading to a better stability but also an increase in the core size.^[79] Phosphines are also exchangeable by an ionic thiol-containing ligand yielding water-soluble AuNPs.^[77] Chechik showed that weakly bound ligands (e.g., short-chain thiolates, amines, sulfides) can be partially replaced from the surface of Au nanoparticles by disulfides. The exchange reaction shows zero-order with respect to the adsorbing disulfide. Interestingly, the two branches of the disulfide molecule do not adsorb close to each other on the surface of Au particle.^[80]

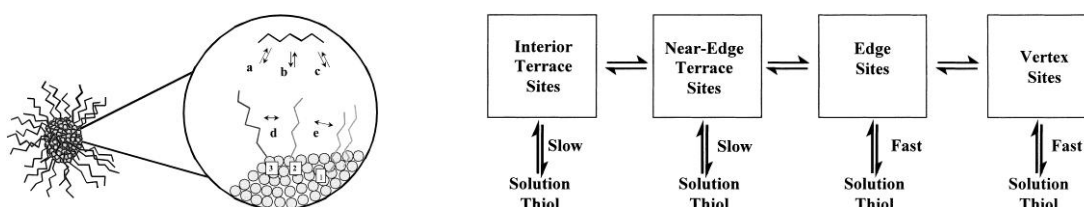


Figure 9 – Cartoons illustrating the ligand place exchange reactions on AuNPs: (a) Exchange of vertices thiolates (3) with solution thiol; (b) Exchange of edge and near-edge thiolates (2) with solution thiol; (c) Exchange of terrace thiolates (1) with solution thiol; (d) Surface migration among vertices and edge thiolates; (e) Surface migration among edge (and near-edge) and terrace thiolates. The gold sites are labeled as: (1) terrace core sites, (2) edge and near-edge core sites; and (3) vertices sites. Taken from Hostetler *et al.*^[81]

Murray and co-workers studied the exchange of thiols by thiols on AuNPs and showed that it is an associative reaction and that displaced thiolate becomes a thiol solution product. Moreover disulfides and oxidized sulfur species are not involved in the reaction.

Cluster-bound thiolate ligands differ widely in susceptibility to place-exchange, presumably owing to differences in binding sites (Au core edge and vertex sites are presumably more reactive than terrace sites; see **Figure 9** for schematic representation). The rate of place-exchange decreases as the chain length and/or steric bulk of the initial protecting ligand shell is increased.^[81] Montalti and co-workers monitored pyrene derivative exchange with decanethiol^[82] and found that it was consistent with Murray's suggested "S_N2"-type associative mechanism.^[81] The presence of two place-exchange kinetic processes is consistent with some degree of surface dishomogeneity, which makes some sites more easily exchangeable than others, a feature that has already been observed by Murray.^[81] The latter showed that not only thiolate ligands are exchanged but this process comes along with the transfer of metal (see schematic mechanism in **Figure 10**). Furthermore, ligand and metal exchange reactions appeared inhibited when conducted under N₂ which implicates the participation of an oxidized form of gold in that process such as Au(I) thiolate.^[83]

Bruce Lennox *et al.* investigated ligand-exchange reactions of 4-(*N,N*-dimethylamino)pyridine-capped gold nanoparticles (DMAP AuNP) with functionalized thiols (RSH). A simple, convenient, and facile synthesis method has been developed. An important feature of this method is its requirement of only very modest quantities of excess thiol ligand. DMAP-AuNPs prove to be versatile precursors for both water- and organic-soluble AuNPs. DMAP is readily displaced by various functionalized thiols ranging from mercaptocarboxylic acids to ferrocene-terminated thiols. UV-Vis spectroscopy and transmission electron microscopy (TEM) confirm that the mean diameter and the size dispersity of the initial DMAP-AuNPs were retained upon ligand exchange. The RS-AuNP thus prepared were efficiently purified by gel permeation chromatography (GPC) with neither residual DMAP nor RSH detected in the final product.^[84]

Murray also used the annealing procedure as follows: The EtOH hexanethiolate ($C_6H_{13}-SH$) soluble MPCs were co-dissolved with an alkanethiol ($C_{16}H_{33}-SH$) in a mole ratio of *ca.* 1:50 (ratio of MPC cores to alkanethiol) in CH_2Cl_2 and allowed to stir for 4 days. The solvent was removed under rotary evaporation (without heating), and the barely dried product was sonicated in acetonitrile for *ca.* 5 min, allowed to settle, and the solvent decanted. The sample was rinsed twice more with acetonitrile (which removes the thiol) and allowed to dry in the hood. This very gentle procedure constitutes what it is called an annealing reaction. Whetten *et al.*^[74, 88] also observed a narrowing of the dispersity of alkanethiolate-coated MPCs, using a similar procedure but with much higher thiol concentrations and with heating. Thus far, they have obtained similar results using alkanethiolate rather than thiol (thiolate prepared in situ by mixing equimolar thiol and potassium tertiary butoxide) or another thiol such as hexanethiol (C_6-SH). No change in dispersity is seen when the thiol is omitted from the annealing solution. There is some variability in the success of the annealing procedure, in terms of differences in residual dispersity in different batches of annealed MPCs. Also annealing yields a less dramatic improvement in monodispersity when carried out on the ethanol-insoluble fraction of MPCs.

The kinetics of exchange of phenylethanethiolate ligands (PhC_2S) of monolayer-protected clusters (MPCs, average formula $Au_{140}(PhC_2S)_{53}$) by para-substituted arylthiols (*p*-X-ArSH) are described by Murray and co-workers.^[89] 1H NMR measurements of thiol concentrations show that the exchange reaction is initially rapid and gradually slows almost to a standstill. The most labile ligands, exchanging at the shortest reaction times, are thought to be those at defect sites (edges, vertices) on the nanoparticle core surface. The pseudo-first-order rate constants derived from the first 10% of the exchange reaction profile vary linearly with in-coming arylthiol concentration, meaning that the labile ligands exchange in a second-order process, which is consistent with ligand exchange being an associative process. A linear Hammett relationship demonstrates a substituent effect in the ligand place exchange reaction, in which the bimolecular rate constants increase for ligands with electron-withdrawing substituents ($X = NO_2$ and 4-OH). This is interpreted such that the more polar Au-S bonds at the defect sites favor bonding with more electron deficient sulfur moieties. At longer reaction times, where ligands exchange on non-defect (terrace) as well as defect sites (**Figure 11**), the extent of ligand exchange is higher for thiols with more electron-donating substituents. The difference between

short-time kinetics and longer-time pseudo equilibria is rationalized based on differences in Au-S bonding at defect vs. non-defect MPC core sites.

Murray asked an interesting question: does core size matter in the kinetics of ligand exchanges of monolayer-protected Au clusters?^[90] He answered by comparing the kinetics of exchanges of phenylethanethiolate ligands (PhC₂S-) of the monolayer-protected clusters (MPCs) Au₃₈(SC₂Ph)₂₄ and Au₁₄₀(SC₂Ph)₅₃ with *p*-substituted arylthiols (*p*-X-Ar-SH), where X = NO₂, Br, CH₃, OCH₃, and OH. First-order rate constants at 293 K for exchange of the first *ca.* 25% of the ligands on the molecule-like Au₃₈ MPC, measured using ¹H NMR, vary linearly with the incoming arylthiol concentration; ligand exchange is an overall second-order reaction. Remarkably, the second-order rate constants for ligand exchange on Au₃₈ are very close to those of corresponding exchange reactions on the larger nanoparticle Au₁₄₀ MPCs. These results quantitatively show that the chemical reactivity of different sized nanocrystals is almost independent of size; presumably, this is because the locus of the initial ligand exchanges is a common kind of site, thought to be the nanocrystal vertices. The rates at later stages of exchange (beyond *ca.* 25%) differ for Au₃₈ and Au₁₄₀ cores, the latter being much slower presumably due to its larger terrace-like surface atom content. The reverse exchange reaction was studied for Au₃₈ MPCs, where the incoming ligand is phenylethanethiol. Remarkably, the rate constants of both forward and reverse exchanges display identical substituent effects, which imply a concurrent bonding of both incoming and leaving ligands to the Au core in the rate-determining step, as in an associative mechanism. X = NO₂ gives the fastest rates, and the ratio of forward and reverse rate constants gives an equilibrium constant of K_{EQ,PE} = 4.0 that is independent of X.^[90]

Phosphine-stabilized Au₁₁ clusters in chloroform were reacted with glutathione (GSH) in water under a nitrogen atmosphere. The resulting Au:SG clusters exhibit an optical absorption spectrum similar to that of Au₂₅(SG)₁₈, which was isolated as one of the major products from chemically prepared Au:SG clusters.^[91] Rigorous characterization confirms that the Au₂₅(SG)₁₈ clusters were selectively obtained on the sub-100 mg scale by ligand exchange reaction under aerobic conditions. The ligand exchange strategy offers a practical and convenient method of synthesizing thiolated Au₂₅ clusters on a large scale.^[92]

Bruce Lennox and co-workers studied the exchange of linear alkane thiols (C_{10} -SH is replaced by $C_{12}H_{25}$ -SH) and demonstrate that this exchange follows a second-order Langmuir diffusion-limited rate (**Equation 1**).^[93]

$$\Theta(t) = \frac{Ak\sqrt{t}}{1 + k\sqrt{t}}$$

Equation 1 - A is the final fractional coverage, Θ is the fractional surface coverage of the incoming thiol, and k is the rate constant.

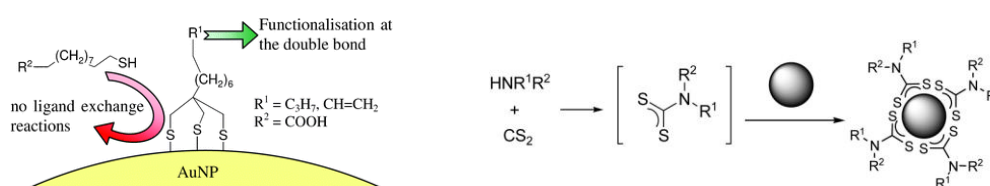


Figure 12 – Schemes showing that the trithiolate ligand prevents further exchange by thiols (on the left, taken from Wojcyskowski *et al.*^[94]) and dithiocarbamate formed by mixing carbon disulfide and secondary amine provides bidentate chelating moieties (on the right, taken from Dubois *et al.*^[95]).

Trithiolates (1,1,1-tris(mercaptomethyl)undecane) were also used to stabilize and functionalize AuNPs (**Figure 12** on the left) and are claimed to be irreplaceable by exchange reactions because of their tripod status leading to a strong bonding to the particle surface ascribed to the chelate effect and to the space saving geometry.^[94] It was also reported that dithiocarbamate ligands can be used in replacement of trioctyl phosphine oxide (TOPO) as stabilizing agent (**Figure 12** on the right) on core-shell CdSe/ZnS nanocrystals.^[95] One might extend the nanocrystal notion to the one of nanoparticles, e.g. AuNPs, assuming that a stronger binding is created if compared to a single thiolate anchorage.

Lee and co-workers reported a study on the stability of dithiol and trithiol derivatives in comparison with a monochelating thiol.^[96] These particles were subjected to cyanide ions and it appeared that while C_{18} -SH-capped AuNPs showed the fastest rate of decomposition, those functionalized with the dithiol were the most resistant to decomposition. At last, the trithiol derivative was less resistant to etching leading to that sorting order for stability: dithiol > trithiol > thiol. Conversely, they established that the conformational order follows this decreasing trend: monothiol > dithiol > trithiol.

Scott and co-workers probed the stability of dithiolate vs. thiolate-capped AuNPs as well as a mixed monolayer of both.^[97] Subjected to oxygen and cyanide, the dithiolate-

stabilized AuNPs were etched at much higher rates than the monothiolate- and mixed-monolayer-stabilized NPs. They came to the conclusion that strategies to increase ligand-metal interactions by incorporating more thiolate linkers into the ligand must also take into account the packing efficiency and/or the stability of such ligands on the metal surface, which can make them much more prone to oxidation under ambient conditions.

2.2.2. New functionalities supplied by ligand exchange

Amide and ester coupling reactions of ω -functionalized monolayer-protected gold cluster molecules (MPCs) are an exceptionally efficient avenue to a diverse variety of polyfunctionalized MPCs starting from a small subset of ω -functionalized materials. Coupling reactions have been employed to produce MPCs bearing multiple copies of different functional groups.^[85]

As discussed earlier, Murray and co-workers studied the kinetics of exchanges on MPCs and they found out that for the first stage of the ligands exchanged the chemical reactivity would be the same independently of the size of MPCs: the initial ligand exchange takes place at vertices. As for the rates of latter stages of exchange, the bigger the cluster is, the slower the exchange rate is because of larger terrace-like surfaces on bigger clusters.^[90]

Besides ligand exchange reactions, direct synthesis approaches have also been employed to prepare functionalized nanoparticles but most of these methods suffer from the incompatibility of functionalized ligands with the reaction conditions and show a strong dependence of the core size on the stabilizing ligand used during synthesis.

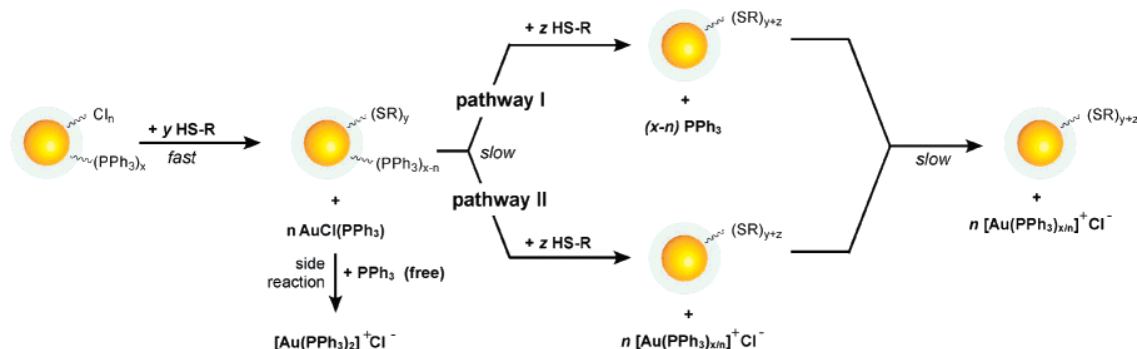


Figure 13 - Proposed three-stage mechanism for the ligand exchange reaction between 1.5-nm Au_n-TPP and thiols. In the initial stage, part of the phosphine ligand shell is rapidly replaced in the form of AuCl(PPh₃) until no more particle-bound chlorides are available. This initial phase is followed by removal of the remaining phosphine ligands either as free PPh₃ in solution (pathway I) or through direct transfer of PPh₃ to closely associated AuCl(PPh₃) (pathway II). During the final stage, the completed thiol ligand shell

is reorganized into a more crystalline state. Although treated as separate stages, it is most likely that the three stages overlap to a certain extent. Taken from Woehrle *et al.* [16]

James Hutchison and co-workers exposed that ligand exchange reactions of 1.5-nm TPP-stabilized nanoparticles (TPP: triphenylphosphine) with ω -functionalized thiols provides a versatile approach to functionalized, 1.5-nm gold nanoparticles from a single precursor. They describe the broad scope of this method and the mechanistic investigation of thiol-for-phosphine ligand exchanges. The method is convenient and practical and tolerates a wide variety of technologically important functional groups while producing very stable nanoparticles that essentially preserve the small core size and size dispersity of the precursor particle. The mechanistic studies reveal a novel three-stage mechanism that can be used to control the extent of ligand exchange. During the first stage of the exchange, $\text{AuCl(PPh}_3\text{)}$ is liberated, followed by replacement of the remaining phosphine ligands as PPh_3 (assisted by gold complexes in solution). The final stage involves completion and reorganization of the thiol-based ligand shell (see **Figure 13**). [16]

James Hutchison reported the same study for Au_{11} clusters: Ligand exchange of phosphine-stabilized undecagold precursor particles, $\text{Au}_{11}(\text{PPh}_3)_8\text{Cl}_3$, with ω -functionalized thiols provides a convenient and general approach for the rapid preparation of large families of thiol-stabilized, subnanometer ($d_{\text{CORE}} \sim 0.8$ nm) particles. The approach permits the rapid incorporation of specific functionality into the stabilizing ligand shell, is tolerant towards a wide range of functional groups, and provides convenient access to new materials inaccessible by other methods. Mechanistic studies and trapping experiments give insight into the progression of the ligand exchange, providing evidence that the core size of the phosphine-stabilized undecagold precursor particles is preserved during ligand exchange. The optical properties of the thiol-stabilized nanoparticles depend strongly on the composition of the ligand shell, and a series of studies suggests that this dependence is a result of the ligand shell's influence on the electronic structure of the particle core, as opposed to a structural change within the nanoparticle core. [98]

Back to 1998, Royce Murray and co-workers studied the steric effects involved in the place exchange reaction [99] and the key findings regarding the steric environment of their monolayer ligand shells are as follows: (i) $\text{S}_{\text{N}}2$ reactions of ω -bromo-functionalized MPCs indicate that selectivity and rate of reaction are jointly controlled by the steric bulk of the incoming nucleophile and the spatial placement of the ω -bromo- reaction center

within surrounding alkanethiolate diluent chains. The reaction retardation observed for submerged ω -bromo-groups may prove to be a useful effect in designing cluster materials that perform substrate-selective transformations; (ii) ω -bromo-functionalized MPCs have reactivity comparable to that of primary alkyl halide monomers (RBr). This result suggests that the utility of S_N2 chemistry on MPCs will not be significantly reduced by the matrix steric hindrance found for 2D SAMs; (iii) The rate of NaCN decomposition decreases with increasing alkanethiolate chain length and steric bulk. This effect levels off for chain lengths greater than C10. Understanding cluster-core decomposition is of course relevant to defining the limitations on synthetic reagents that can be employed in reactions of functionalized clusters; (iv) Infrared spectroscopic studies indicate that MPC alkanethiol ligands have a disorder in cluster solutions that approaches that of liquid alkanes. This result is consistent with the facile solution-phase S_N2 reactivity observed, and further suggests that substantially more complex ligand structures can be accommodated on MPCs. In sum, the results are consistent with a highly mobile MPC ligand environment in which chain packing density decreases at progressively increasing distances from the gold core, and provides encouraging evidence that gold MPCs have potential as massively polyfunctional chemical reagents.^[100]

p-Substituted arylthiols were exchanged from initially phenylethanethiolate-protected Au₃₈ clusters and hexanethiolate-protected Au₁₄₀ clusters and the result reported by Murray *et al.* showed that the introduction of new polar ligands results in the increase of the near-infrared intensities. The latter are systematically larger for thiophenolates ligands having more electron withdrawing substituents.^[101]

Poly(ethylene glycol) (PEG) thiolate ligands, namely HS-C₆-PEG₁₆₃, were exchanged on PhC₂-SH stabilized Au₃₈ clusters by Murray *et al.* and core size was preserved during the exchange.^[102]

Metal nanoparticles can even exhibit a liquid-like behavior provided that a thiol containing ionic liquid was used as a stabilizer. It starts from a derivative ammonium halide and upon exchange of the halide anion for an amphiphilic sulfonate anion, the final gold nanoparticles become liquid-like at room temperature (which was also observed for platinum, palladium and rhodium particles).^[103]

Special functionalities can be brought by ligand exchange, especially in introducing hydrophilic ligands to hydrophobic nanoparticles thus creating the so-called Janus

nanoparticles. Such particles can be prepared by interfacial engineering leading to hydrophobic surfaces and hydrophilic ones located on two separated sides.^[104]

One can also use fluorinated thiol-ligands to obtain totally hydrophobic particles, but in the case of replacement on phosphine-stabilized Au₅₅, the resulting nanoparticle core change.^[105]

Ligand exchange can be applied on more complex systems such as AuNPs initially covered by a polymer – poly(*N*-vinyl-2-pyrrolidone), PVP – further replaced by thiolated 4'-octyloxy-4-cyanobiphenyl groups which gave monodisperse small particles while a photochemical reduction approach led to a bimodal particle size distribution.^[106]

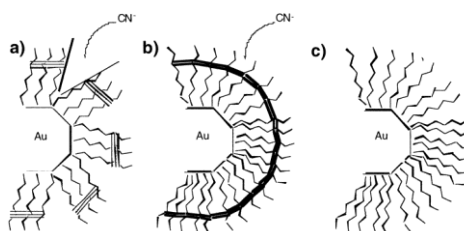


Figure 14 – Illustration of ‘vertex effect’ hypothesis for decomposition rates of amide- and ester-functionalized AuNPs: a) weakly hydrogen-bonded systems; b) strongly hydrogen-bonded systems; c) ester AuNPs. Taken from Paulini *et al.*^[107]

Rotello and co-workers have reported that modifying a thiolate stabilizing ligand by the simple replacement of an amide group with an ester group increased the resistance of the nanoparticles to cyanide-induced decomposition.^[107] They proposed that a ‘vertex effect’ accounted for the difference in decomposition rate. They argued that when amide groups were present, they formed strong hydrogen bonds with one another along the flatter parts of the nanoparticle surface, leaving gaps at the vertices (**Figure 11**), which could be exploited by cyanide ions to decompose the gold core in case of etching (**Figure 14**). However, when ester groups were present, hydrogen bonding was not possible, and the weaker ‘intramonolayer’ interactions gave rise to more uniform coverage across the nanoparticle surface, and consequently greater stability.

By altering synthesis conditions, such as different substrates and solvents, Shon *et al.* controlled both the core size and the monolayer composition of AuNPs.^[12] The composition of the monolayers appeared to be largely determined by thermodynamics. The solvation-driven thermodynamic controls of precursor ligands govern monolayer composition of mixed-monolayer-protected AuNPs generated from mixtures of

alkanethiols and end-functionalized alkanethiols in toluene. Thermodynamic preferential adsorption of long-chain alkanethiolate occurs in THF. MPC formation in THF provided better passivation reactivity of ligands during the nucleation-growth-passivation process.

2.2.3. Means of purifying mixed monolayer-protected gold nanoparticles

Size exclusion chromatography was used as a way to purify the esterified gold nanoparticles obtained in this work. Indeed the difference of weight between the AuNPs and the esterified-to-be molecules is large enough to have a well-defined separation: for example 2 nm-(C₁₂H₂₅-SH)-stabilized AuNPs (inorganic/organic ratio 80:20) is about 60 kg.mol⁻¹ and a first generation thiolated cyanobiphenyl ligand is about 1.5 kg.mol⁻¹ resulting in a weight ratio close to $M_{\text{AuNPs}}/M_{\text{ligand}} = 40$.

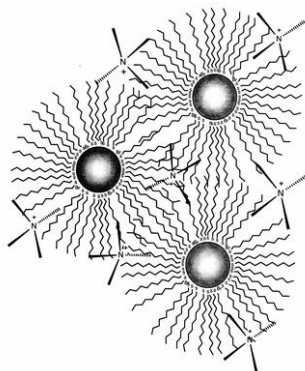


Figure 15 – Schematic diagram showing the stabilization of the solid phase of the nanoparticles due to the presence of TOAB. Taken from Waters *et al.*^[33]

One of the major problems in alkanethiol derivatized gold nanoparticles obtained with Brust's biphasic method – in addition of the alkanethiol in excess amount – is the presence of a phase-transfer agent that is retained as a persistent impurity. Indeed it was proposed that both the quaternary ammonium ion and the bromide are incorporated within the ligand shell creating electrostatic interaction between particles (**Figure 15**). Moreover alkyl chains of both the capping agent and the tetraoctylammonium (TOA⁺) can interact because of alkyl chain interdigitation.^[108] Back to 2003 Schiffrin's group described how the Soxhlet extraction with acetone^[33] could purify such particles but a 12 hour-procedure does not seem to be the least time-consuming one.

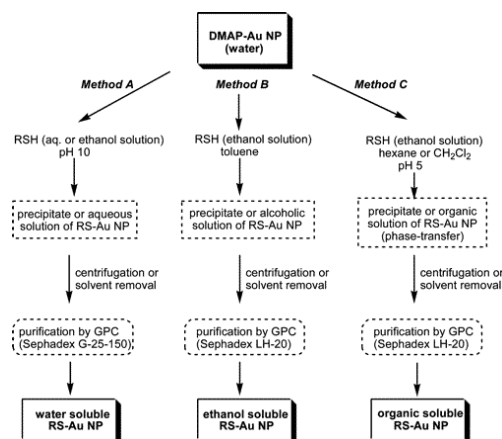


Figure 16 – The different synthesis ways proposed by Lennox *et al.* and consequent purifications means depending on the solubility of final particles. Taken from Rucareanu *et al.*^[84]

Lennox *et al.* proposed different pathways to synthesize 4-(*N,N*-dimethylamino)pyridine-protected gold nanoparticles (DMAP-AuNP) followed by ligand exchange by thiols and finally need to purify particles.^[84] Size exclusion chromatography was used and depending on the solubility of particles, gel filtration (Sephadex G25-150 for hydrophilic samples) or gel permeation (Sephadex LH-20 for lipophilic samples) was performed (see **Figure 16**).

James Hutchison *et al.* reported the purification and the size separation of AuNPs *via* diafiltration^[32] (see **Figure 4**). Indeed nanoparticle samples require sufficient purification which can often be more challenging than the preparation itself, involving tedious, time-consuming, and wasteful procedures such as extensive solvent washes and fractional crystallization. Various standard separation/purification techniques were analyzed. A rigorous combination of extraction with CH₂Cl₂ was carried out, as well as Sephadex chromatography, and ultracentrifugation. A second approach, dialysis, has also been compared for purification. Dialysis is advantageous due to the fact that purification can be carried out with water alone. Despite an improvement in purity over the literature method,^[109] these two approaches had some drawbacks that needed to be addressed: (1) Extractions are not generally applicable for the removal of free ligand, especially when the solubilities of the ligand and ligand-stabilized particle are similar. Additionally, while the volume of organic solvent used has been reduced, a more toxic halogenated solvent has been employed. (2) The 3-nm nanoparticles tend to irreversibly bind to the Sephadex chromatography support, decreasing the yield and limiting reuse of the chromatographic material. (3) Ultracentrifugation can be difficult or impractical on larger scales and

requires a significant time investment, increasing the time required for preparation of nanoparticle samples to 3 days. (4) Dialysis produces a large amount of aqueous waste and requires a significant time investment.

After synthesis (estimated to require around 3h in original Brust's synthesis^[1]), the raw product is obtained by successive evaporation, suspension, filtration, washing, dissolution steps as described in the original Brust's procedure.^[1] More precisely the crude product solution is evaporated in a rotary evaporator and then mixed in ethanol thus forming a suspension. After the solution was kept at low temperature, the dark brown precipitate is filtered off and washed with ethanol. The residue is re-dissolved in toluene and the procedure is repeated until the product shows no trace of free material.

Triphenylphosphine-protected AuNPs are washed with a series of solvents (hexanes, saturated sodium nitrite and a 2:3 methanol:water mixture) to remove the phase transfer catalyst, byproducts, and unreacted starting materials. Further purifications by precipitation from chloroform upon slow addition of pentane (typically 2-3 precipitations) removed Au salts such as $\text{AuCl}(\text{PPh}_3)$.^[5]

In the case of diglyme-protected AuNPs a standard centrifugation and redispersion was performed to have the particles cleaned.^[18]

The crude product in Brust's one-phase synthesis is thoroughly washed with diethyl ether to remove excess *p*-mercaptophenol. After evaporation of the diethyl ether the material was washed with water to remove borates and acetates, dissolved in propan-2-ol and dried over Na_2SO_4 .^[110]

Aliphatic thiols with tunable length were synthesized by reacting alkyl bromide with hexamethyldisilathiane under a mild condition and to be used as stabilizing agent according to Brust's two-phase synthesis. As usual particles prepared with these thiols were precipitated with ethanol and were filtered over Millipore filter paper (0.5 mm pore size).^[111]

2.3. Results and discussion

The aim of this following paragraph is not to give extensive explanations on a relatively well-known and widely used reaction but rather to bring a rapid overview on the directions we chose in order to use the described AuNPs as starting material in subsequent exchange or esterification reactions (both the latter are presented in the next chapter, see chapter 3 *LC Dendrimer-functionalized AuNPs*).

2.3.1. Direct synthesis

2.3.1.1. With alkanethiols

Gold nanoparticles were synthesized according to a modified protocol from the original Brust's *et al.* biphasic procedure.^[1] Experimental details are depicted in order to make these results reproducible and as comprehensive as possible.

Typically, a 20 ml aqueous solution containing 300 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (1.0 equiv., $7.62 \cdot 10^{-4}$ mol) was mixed to an 80 mL toluene solution containing 1.416 g of TOAB (3.4 equiv., $2.59 \cdot 10^{-3}$ mol). Thanks to the phase-transfer agent, the gold salt is transferred to the organic phase – the colorless organic phase becomes orange and the yellow aqueous phase becomes colorless – and the aqueous phase is subsequently removed. The reaction takes place according to the experimental scheme presented in **Figure 17**.

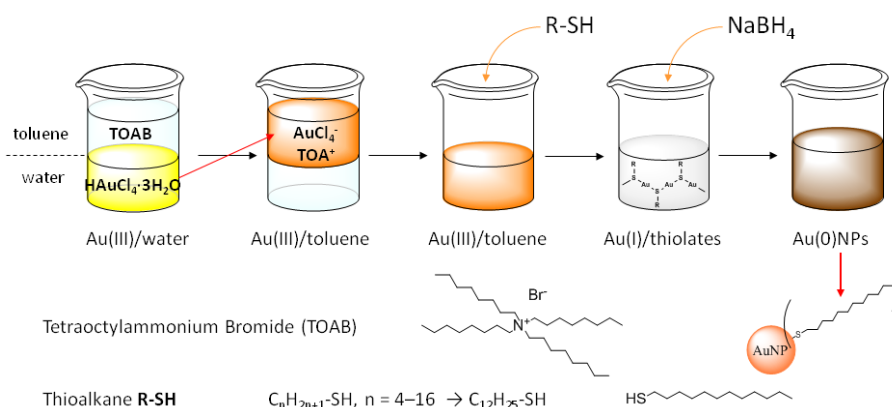


Figure 17 – Sketch of the biphasic reaction according to Brust's protocol. Au(III) is transferred from water to the organic phase, forms Au(I)/thiolates polymers when thiols are added and are reduced by sodium borohydride to yield ($\text{C}_{12}\text{H}_{25}\text{-SH}$)-stabilized Au(0) nanoparticles according to a nucleation-growth-passivation mechanism.

Once gold is transferred to the organic phase and the water phase is removed, a thioalkane is added: 670 μL of dodecanethiol ($\text{C}_{12}\text{H}_{25}\text{-SH}$, 4.3 equiv., $3.28 \cdot 10^{-3}$ mol) and was kept for stirring vigorously until the organic phase turns from cloudy white to colorless in 10 up to 40 min, both coloration and time depending on the length of the alkane chain (various chain lengths were tested starting from butanethiol up to hexadecanethiol). The discoloration of the orange toluene phase reflects the reduction of Au(III) stabilized by the phase transfer agent into Au(I). Indeed Au(I)-SR polymers are formed from Au(III) ions and thiol RSH. This step is followed by the chemical reduction of Au(I)-SR by 346 mg of a freshly prepared sodium borohydride 10 mL ice-cold aqueous solution (12 equiv., $9.14 \cdot 10^{-4}$ mol/L). The solution was kept under stirring for 3 h before the raw solution was washed thrice with 100 mL of water to stop the reaction and remove most of the excess borohydride salts remaining in the solution. Then toluene was evaporated under reduced pressure at a temperature that should not exceed 40°C for particle stability reasons. The dark residue is suspended into methanol (MeOH) and kept at low temperature in the fridge during a few hours. The suspension is then transferred onto a filtration membrane (Sartorius regenerated cellulose membrane with a $0.2\text{-}\mu\text{m}$ pore size) to be purified through five times alternatively 100 mL of ethanol (EtOH) followed by 100 mL of acetone to remove borohydride salts, excess thiols and thiolate salts, tetraoctylammonium salts and gold salts. The dark powder is redissolved through the filtration membrane with n-heptane – it was found after analysis that accompanying the redissolution of particles in n-heptane, TOAB partly remains on the filtration membrane – and afterwards evaporated to perform the washing steps twice more. The dark powder, possibly presenting a waxy aspect, is dried under high vacuum before further analyses (a representative NMR spectrum is shown in **Figure 18**).

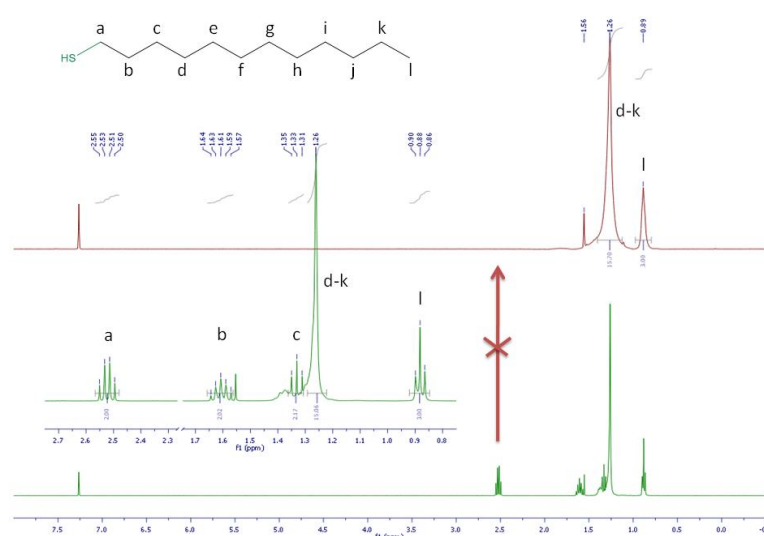


Figure 18 – ^1H -NMR spectra of $\text{C}_{12}\text{H}_{25}\text{-SH}$ ligand (bottom) and the corresponding NPs $\text{Au/C}_{12}\text{H}_{25}\text{-SH}$. The signals corresponding to the methylenes and to the methyls are considerably broadened. The 2.52 ppm (C_aH_2) and 1.61 (C_bH_2) ppm signals have disappeared and the 1.33 ppm one (C_cH_2) is considerably lowered in the foot of the methylene peak. The inset magnifies the signals from the $\text{C}_{12}\text{H}_{25}\text{-SH}$ ligand (the 1.56 signal in both spectra corresponds to the water residue present in CDCl_3).

Different syntheses were made from various chain length alkanethiols $\text{C}_n\text{H}_{2n+1}\text{-SH}$ ($n = 4, 6, 8, 10$ and 12) using exactly the same reaction conditions as well as purification methods; indeed decreasing the chain length could favor the ligand place exchange (easier access to the particle surface) or could decrease the steric hindrance around the functional groups (at the end of a longer alkane chain) introduced *via* a subsequent ligand exchange reaction. Representative TEM images are shown in **Figure 19**.

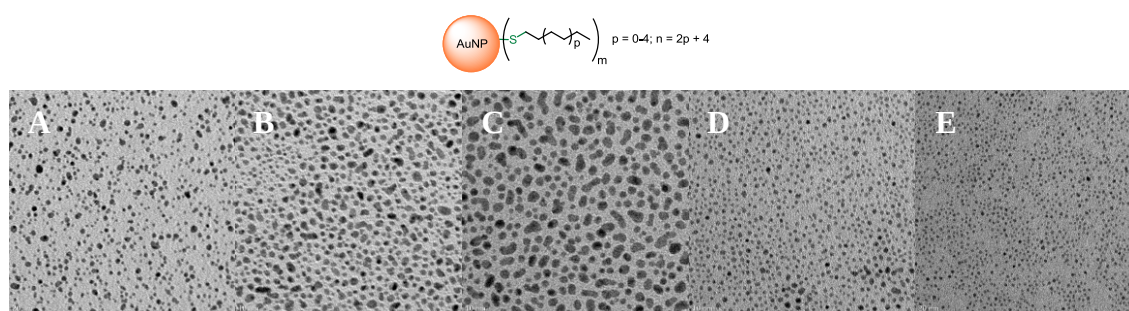


Figure 19 – TEM micrographs of $\text{Au/C}_n\text{H}_{2n+1}\text{-SH}$; $n = 4, 6, 8, 10, 12$. Image analyses revealed different size and size distribution under the same reaction and purification conditions. (A) $n = 4$, 3.27 ± 1.18 nm; (B) $n = 6$, 3.10 ± 1.34 nm; (C) $n = 8$, 3.14 ± 1.63 nm; (D) $n = 10$, 1.83 ± 0.79 nm; (E) $n = 12$, 1.98 ± 0.54 nm.

As noticed in **Figure 19**, it was found that the same reaction and purification conditions did not lead to the same particles and size distributions. The only varying parameter is the

alkanethiol chain length (related to its molecular weight) and the mean diameter and size distribution decrease when the chain length increases as a general trend.

In addition, the proportion of the organic shell expectedly increases with n (concomitantly increasing the molecular weight) as shown by TGA analyses in **Figure 20**.

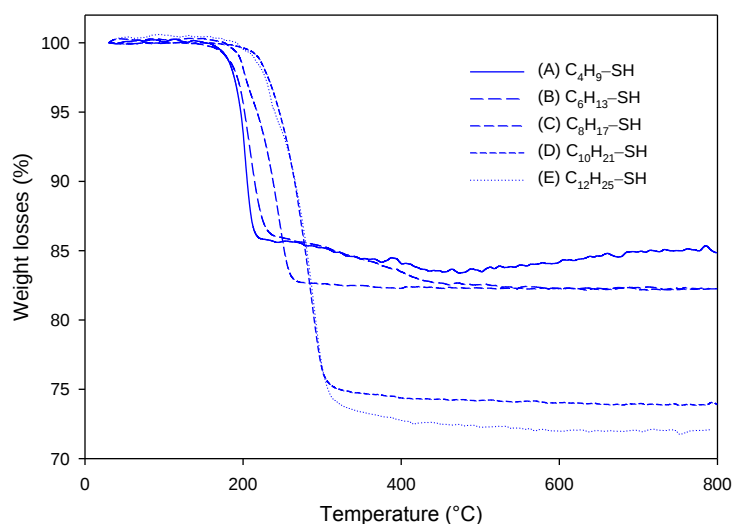


Figure 20 – Thermogravimetric analyses on AuNPs capped with different chain length alkanethiols $C_nH_{2n+1}-SH$ ($n = 4, 6, 8, 10$ and 12). The relative weight losses are attributed only to the organic shell, the proportion of which is: (A) $n = 4$, $\chi_{org} = 16.462\%$; (B) $n = 6$, $\chi_{org} = 17.348\%$; (C) $n = 8$, $\chi_{org} = 17.666\%$; (D) $n = 10$, $\chi_{org} = 25.528\%$; (E) $n = 12$, $\chi_{org} = 27.508\%$.

One can notice a different behavior between the C_4 - C_8 group and the C_{10} - C_{12} one. This is mainly due to the fact that for bigger particles (> 3 nm for the C_4 - C_8 group) a greater proportion of terrace sites are present with respect to the edge and vertex sites. This is probably the reason why there are two different slopes for C_4 and C_6 ((A) and (B) respectively in **Figure 20**), the alkanethiols at vertices, edges and a close proximity of them are degraded at a faster rate than those in the middle of the 111 faces.

Moreover the temperature dependence of the weight losses indicates that the thermal stability of the alkanethiol-stabilized AuNPs increases with increasing chain length which is consistent with Murray's observations.^[35]

These results are summarized in **Table 2** and provide in particular the estimated number of ligands per particle (important in the case of ligand exchange) and γ the coverage of the particle surfaces. One can notice the high values obtained for C_4 and C_6 , the first one being experimentally impossible and the second one being higher than the commonly observed values. Due to the broad size distributions of the samples, these calculated

values reflect an average of observations and the smaller particles presenting a higher proportion of ligands are thus not considered according to a balanced average. Finally these results will not be considered in the following lines.

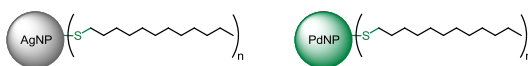
Particles	Diameter (nm)	σ_{abs} (nm)	σ_{rel} (%)	# atoms _{core}	# atoms _{surface}	χ_{org} (%) fr. TGA	MW(C _n -SH)	# ligand _{shell}	γ_{coverage}
Au/C ₄ -SH	3.27	1.18	36.1	1062	388	14.10	90.19	457	1.18
Au/C ₆ -SH	3.10	1.34	43.2	905	345	13.52	118.24	316	0.92
Au/C ₈ -SH	3.14	1.63	51.9	940	354	17.67	146.29	272	0.77
Au/C ₁₀ -SH	1.83	0.79	43.2	186	103	25.53	174.35	72	0.70
Au/C ₁₂ -SH	1.98	0.54	27.3	236	125	27.51	202.40	87	0.70

Table 2 – Au/C_n-SH comparison through the various characteristic parameters of sizes, number of atoms (# atoms) and ligand coverage on AuNP surface. These approximations were calculated according to the spherical core model^[35] and do not reflect the particle shapes.

First there are two groups C₈ and C₁₀-C₁₂, both are considerably differing by their size and size distribution. They present more than 900 Au atoms or less than 250 atoms in their core and ~350 or ~100 respectively on their surface. The coverage is in the 0.7 range which correlates with the commonly observed values of $\gamma = 0.66$ for C₁₂H₂₅-SH.^[35] Secondly, considering the size distributions, only the C₁₂ sample shows a distribution lower than 30 % which seems to represent a limit for this synthesis type under the adopted conditions. Finally this value will be considered as acceptable in the subsequent experiments involving aliphatic chains and was decreased in post-purifications with size exclusion chromatography following a ligand exchange reaction (2.3.2 or 3.4.1).

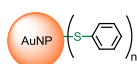
As a consequence, these results taken into account, most of the syntheses involving alkanethiols in the following experiments (for ligand exchange in particular) were done with dodecanethiol that presents in addition multiple advantages if compared with the other thiol analogues: due to its wide use, C₁₂H₂₅-SH is among the cheapest thiols, it is more convenient to handle as it is in the liquid state, it is less volatile than its shorter analogues, and it is one of the most stable Au-SR combinations along with hexanethiol and butanethiol (both the latter are not the most convenient to handle).^[112]

With a view to have a comparison point, NPs from other metals were synthesized: silver nanoparticles (AgNPs) and palladium nanoparticles (PdNPs) presented in **Scheme 2**.



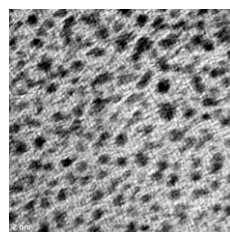
Scheme 2 - Ag/C₁₂H₂₅-SH and Pd/C₁₂H₂₅-SH were synthesized according to a modified Brust's procedure basically replacing the gold salts by silver and palladium precursors respectively.

It consists in the use of silver salts (Ag^I trifluoroacetate) and palladium salts (Pd^{II} acetate) in a modified Brust's procedure proposed by Zheng *et al.*^[23] It yielded 1.6 ± 0.7 nm AgNPs and 1.46 ± 0.47 nm PdNPs. These particles were afterwards subjected to a ligand place exchange reaction with G₁CB-SH dendron and results of their assemblies on surfaces are presented in chapter 4.3.3.



Scheme 3 - AuNPs stabilized by benzenethiol (BT), the steric bulk of which favors small particle sizes.

The aliphatic thiols were not the only ones investigated but aromatic ones (benzenethiol, BT, see **Scheme 3**) seemed at first promising candidates for small particles sizes: the higher steric hindrance of the aromatic core, if compared to the aliphatic chains, shall promote particles with a high curvature surface, i.e. small particle diameters. On the one hand particles have a mean diameter of 1.26 ± 0.27 nm but a large number of aggregates (~50 nm) are also present. Due to the close proximity of the ligand to the NP surface plus the difference of binding sites, the ¹H-NMR spectra displayed very broad signals and signal multiplicity (e.g. Whetten *et al.*^[113, 114]). The use of BT in direct synthesis was consequently abandoned to the benefit of its use as 'diluent' agent along with 4-mercaptophenol (pMP).



Scheme 4 – AuNPs stabilized by triphenylphosphines to be subsequently completely exchanged by thiols, as a source of small and nearly monodisperse AuNPs (the scale bar is 2 nm).

The last direct approach was the one proposed by Hutchison *et al.*^[5, 16, 43, 98, 115] starting from phosphine-stabilized AuNPs (see **Scheme 4**), the phosphines being totally replaced

by thiols in a ligand exchange reaction. This is possible because of the weaker stabilization of AuNPs by phosphines if compared to the strong-binding thiols. Nevertheless the particles formed were not found enough stable in the following steps of ligand exchange probably due to their small size (1.52 ± 0.37 nm, see **Scheme 3**) which make them much more prone to oxidation due to higher curvature and concomitant less dense packing of alkanethiols.

2.3.1.2. With ω -functionalized thiols

Aliphatic as well as aromatic HO-functionalized AuNPs were investigated with a view to use them in esterification reactions.

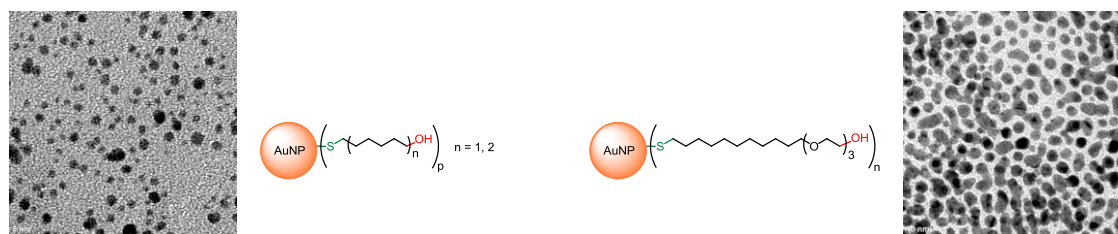


Figure 21 – ω -hydroxyalkanethiols and triethylene glycolalkanethiols led to NPs (Au/HS- C_6 -OH; Au/HS- C_{11} -OH and Au/mud3eg respectively) surrounded by available -OH groups ready for esterification. On both sides TEM images show the large particle size distribution (left: Au/HS- C_6 -OH; and right: Au/mud3eg).

C_6 and C_{11} alkane chains end-functionalized by an -OH group were investigated (see **Figure 21**). The NPs were synthesized according to the Brust's monophasic method.^[110] Unfortunately, the syntheses led to rather big particles with a large size distribution (see TEM images in **Figure 21**: left Au/HS- C_6 -OH, 2.07 ± 0.94 nm; and right: Au/mud3eg, 3.39 ± 1.93 nm) and some big aggregates (not shown).

Conversely, when Brust's monophasic synthesis is performed with the original 4-mercaptophenol ligand (pMP), provided that the ligand/Au ratio is increased, very small particle sizes are reached (see TEM micrographs in **Figure 22**).

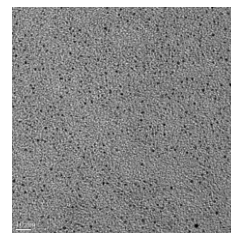
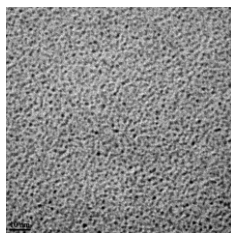
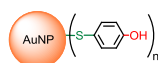
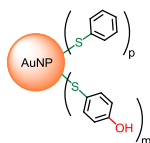


Figure 22 – AuNPs synthesis according to Brust's monophasic method. NPs are stabilized by pMP (Au/pMP) and yield very small particle sizes. TEM images resulting from two different batches: in the middle NPs are 1.22 ± 0.28 and on the right they are 1.00 ± 0.23 nm (the scale bars are 10 nm).

Once again it seems that the steric hindrance helped in the access to the low particle size and size distribution. The –OH group does not seemingly have as much influence as it has for the aliphatic chains (compare non-functionalized and end- functionalized AuNPs in **Figure 19-E** and in **Figure 21** respectively as well as the aliphatic and aromatic HO-functionalized AuNPs in **Figure 21** and **Figure 22** respectively). Hence, the need of having end-functionalized small AuNPs implies the use of aromatic derivatives but it works also for aliphatic derivatives, however leading to high polydispersity.

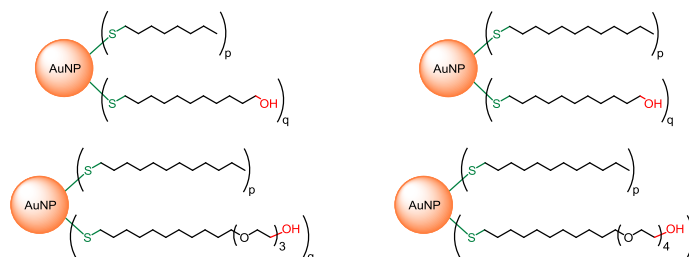


Scheme 5 – Au/BT|pMP: Approach of the mixed aromatic monolayer on AuNPs from a direct synthesis. Here BT is used as a 'diluent' molecule to limit the number of functional groups around the AuNPs.

Considering the dendritic candidates for esterification (size (generation), steric bulk), it was decided to limit the available functional groups to avoid a too large number of unreacted alcohol functions. Therefore BT ligand and pMP were used as a mixture to run a direct reaction; BT was introduced as 2:1 and 1:1 in the mixture (**Scheme 5**). However, the ligands are too similar to be able to estimate the proportion of both in the $^1\text{H-NMR}$ spectrum. Indeed the incoming amount of ligands does not generally reflect the proportion of tethered ligands on the AuNPs. The reactivity of the ligand bearing the functional group is quite different from that of the 'naked' ligand, the whole reactivity also depending on the solvent polarity (e.g. Shon *et al.*^[12, 116]).

2.3.2. Ligand exchange

As mentioned previously (see 2.2.2), the ligand exchange reaction allows one to preserve the size and size dispersion of the initial particles while adding new features. This is what we realized with ligands functionalized by alcohol moieties to be used subsequently in combination with dendrons (see **Scheme 6**).



Scheme 6 – Structure of AuNPs resulting from a ligand exchange reaction on initial hexanethiol- or dodecanethiol-stabilized AuNPs. This led to mixed-monolayer protected NPs: Au/C₈H₁₇–SH±HS–C₁₁H₂₂–OH, Au/C₁₂H₂₅–SH±mud3eg, Au/C₁₂H₂₅–SH±HS–C₁₁H₂₂–OH, and Au/C₁₂H₂₅–SH±mud4eg.

After the synthesis of Au/C₁₂H₂₅–SH as described in the first section of this result part (see 2.3.1.1), HO-functionalized aliphatic alkanethiols were introduced. The example of Au/C₁₂H₂₅–SH±mud3eg is given as an illustration of the determination of ligand ratio after the exchange reaction and purification by Sephadex LH-20 (see Appendix 1) size exclusion chromatography.

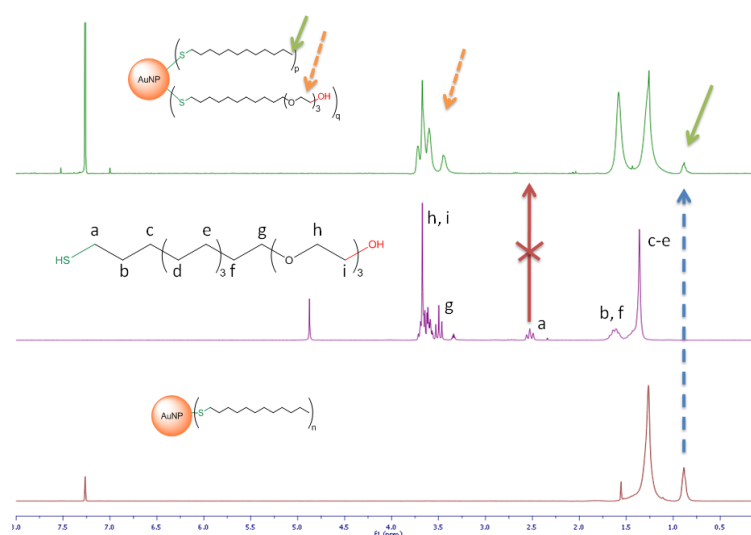


Figure 23 – ¹H-NMR spectra of: Au/C₁₂H₂₅–SH (bottom, in CDCl₃) that were subjected to a ligand exchange reaction with mud3eg (middle, in CD₃OD) leading to particles Au/C₁₂H₂₅–SH_{0.3}±mud3eg_{0.7} (top, in CDCl₃) which ratio was determined from the integrals of the signals under arrows. Note that C_aH₂ signal from mud3eg disappeared after ligand exchange on AuNPs and purification.

The ligand ratio can be estimated from the ^1H -NMR spectra of both the NPs and the ligands (see **Figure 23**). The following results can be extracted (see also Second appendix): Au/C₁₂H₂₅-SH, ^1H NMR (400 MHz, CD₃OD) δ 3.67 (m, 8H), 3.58 (m, 4H), 3.49 (t, J = 6.5, 2H), 2.51 (t, J = 7.0, 2H), 1.61 (m, 4H), 1.34 (s, 14H); mud3eg ligand: ^1H NMR (400 MHz, CD₃OD) δ 3.72 – 3.62 (m, 8H), 3.62 – 3.54 (m, 4H), 3.49 (t, J = 6.5, 2H), 2.51 (t, J = 7.0, 2H), 1.72 – 1.51 (m, 4H), 1.34 (s, 14H); Au/C₁₂H₂₅-SH $\pm$ mud3eg: ^1H NMR (400 MHz, CDCl₃) δ 3.67 (t, J = 24.3, 11H), 3.45 (s, 2H), 1.58 (s, 11H), 1.26 (s, 15H), 0.88 (s, 0.85H). As a result, the top spectrum in **Figure 23** was integrated according the mud3eg ligand and the integration of the methyl peak at 0.88 ppm is different from the one expected. Thus, fast calculations allow one to find a ratio of 3:7 of C₁₂H₂₅-SH (26 ligands) and mud3eg (61 ligands) respectively.

Scope and limitations

Gold nanoparticles have been synthesized according to the Brust's biphasique method by using alkanethiols. A brief study allowed one to choose dodecanethiol as ligand model for the rest of our experiments. Although the phosphine approach was really interesting, their small particle size made them hard to characterize (TEM) and considerably decrease their stability (exchange). On the other hand it was possible to introduce aliphatic or aromatic bearing functional groups (–OH in our study) in a direct or indirect way (by ligand exchange).

Particles that do not present functional groups will be used during the exchange reaction to introduce dendritic ligands and particles presenting –OH moieties will be tested during esterification reactions with dendrimers as will be discussed in the following chapters.

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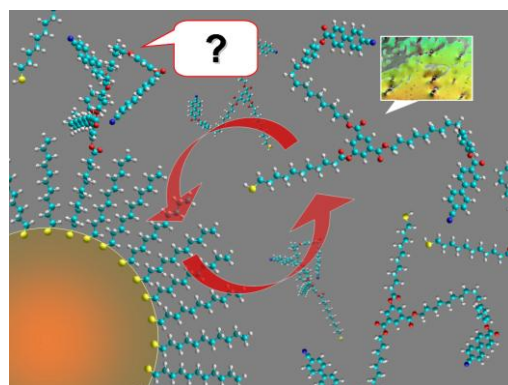
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3. LC Dendrimer-functionalized AuNPs



Schematic illustration of a ligand exchange reaction between $C_{12}-SH$ and $LC-G_1-SH$: The question of the preservation of the dendron mesomorphic properties once anchored on the particle arises

3.1. AuNPs and dendrimers coupling

Many ways to combine AuNPs and dendrimers are reported in the literature. Starting from the simple mixture of both the AuNPs and the dendrimers, various strategies were developed to have them coupled together.

Poly(amido amine) (PAMAM) dendrimers were used as templates where tetrachloroauric acid is reduced to form AuNPs: dendrimer encapsulate the colloids, imparting stability to the aqueous colloidal solution. The dendrimer generation used in the synthesis controls the size of the resultant colloids;^[1] Chechik and Crooks reported that the flexible dendrimers arrange themselves so as to maximize the number of Au/thiol interactions;^[2] Gröhn *et al.* showed that lower generation dendrimers aggregate when stabilizing the metal particles formed, dendrimers of generation 6-9 can template one gold colloid per dendrimer molecule, the size of which is well-controlled by the number of gold atoms added per dendrimer,^[3] as well as other groups.^[4-6] An account from Chechik, Crooks *et al.* reports the synthesis, characterization and applications in metallodentritic catalysis of such PAMAM/metal nanoparticles named dendrimer-encapsulated (metal) nanoparticles (DEMNs or DENs).^[7, 8] AuNPs can be extracted from the interior of PAMAM dendrimers with the use of *n*-alkanethiols extractants, but a 100-fold excess is required to prevent aggregation during extraction,^[9] or alternatively using a selective extraction approach in a water/hexane biphasic system.^[10]

Majoral and co-workers reported metallodendrimers that consist in dendrimers, the periphery of which is grafted of gold clusters mainly through N-Au or P-Au interactions.^[11] Schmid and Majoral showed that a thiol-terminated 4th generation dendrimer (presenting 96 -SH groups)^[12] in the presence of the Au₅₅(PPh₃)₁₂Cl₆ cluster results in the formation of bare Au₅₅: the dendrimer does not only remove the phosphine and chlorine ligands but also acts as a matrix for crystal growth forming then superstructures of Au₅₅.^[13]

Müllen and co-workers found that polyphenylene dendrimers with thiomethyl groups act as templates for AuNPs formation; however the particles have a very broad size distribution impeding a highly ordered assembly.^[14] They presented as well polyphenylene, poly(propyleneimine) and PAMAM dendrimers that were used to cross-link AuNPs finally forming thin films capable of vapor-sensing.^[15, 16]

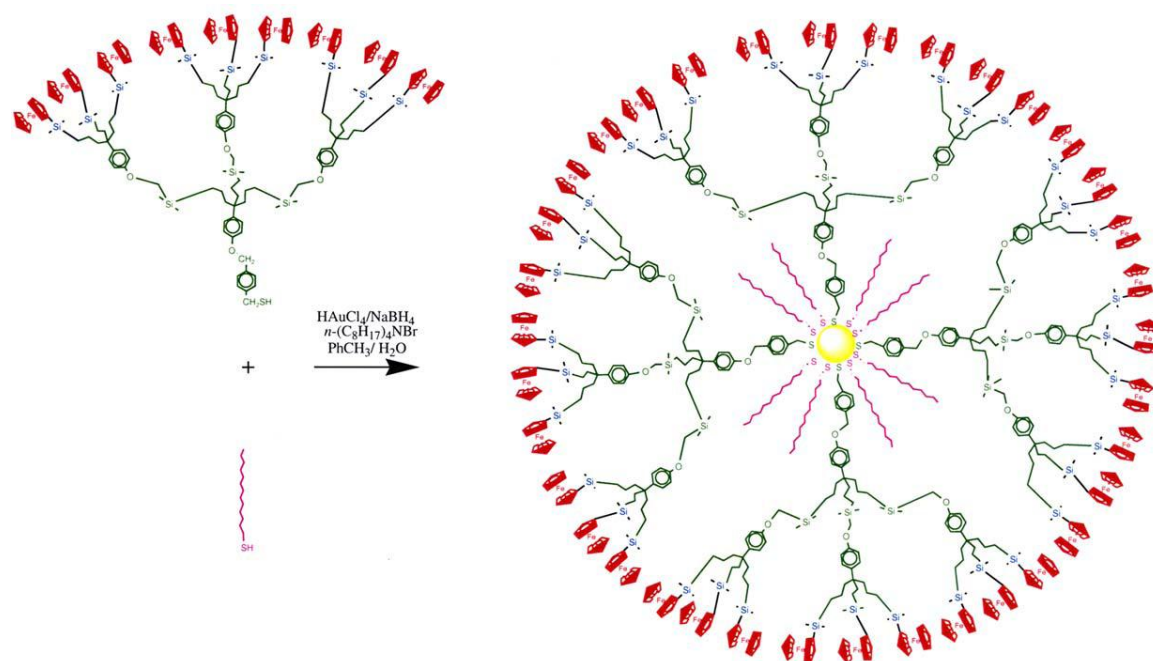


Figure 24 – Tris-silylferrocenylalkylthiol dendrons yielded gold nanoparticle-cored dendrimers containing up to about 200 ferrocenyl groups at the dendrimer periphery. Taken from Labande *et al.*^[17]

Another approach was detailed by Astruc and co-workers: tris-amidoferrocenylalkylthiol dendrons or tris- and nona-silylferrocenylalkylthiol were subjected to a direct Brust synthesis reaction forming mixed systems of AuNPs for electrochemistry applications (**Figure 24**).^[17]

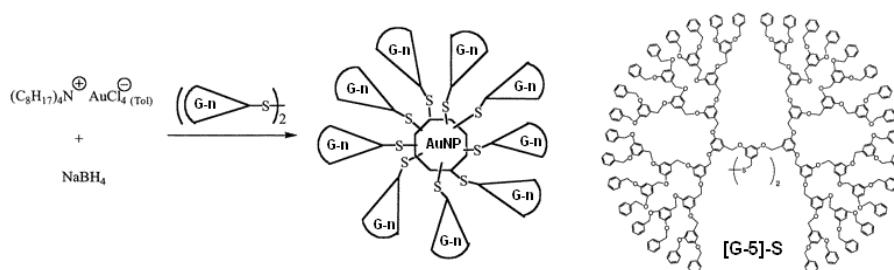


Figure 25 – Nanoparticle-cored dendrimers are obtained by Brust's biphasic method in the presence of Fréchet-type polyaryl ether dendritic disulfide as stabilizers. The synthesis pathway is shown on the left and a 5th generation disulfide is presented on the right as an example. Adapted from Gopidas *et al.*^[18]

In 2003, Gopidas *et al.* discussed the synthesis and characterization of nanoparticle-cored dendrimers (NCDs) as a new group of dendrimers (**Figure 25**). Their conclusions correspond to previous studies: an increasing generation of dendrimer led to a decreasing interaction with the AuNPs surface and because of a large fraction of the surface area is unpassivated, high generation NCDs are thus candidates for catalysis applications.^[18] They reported Pd-G3 NCDs catalytic activity in Heck and Suzuki reactions.^[19]

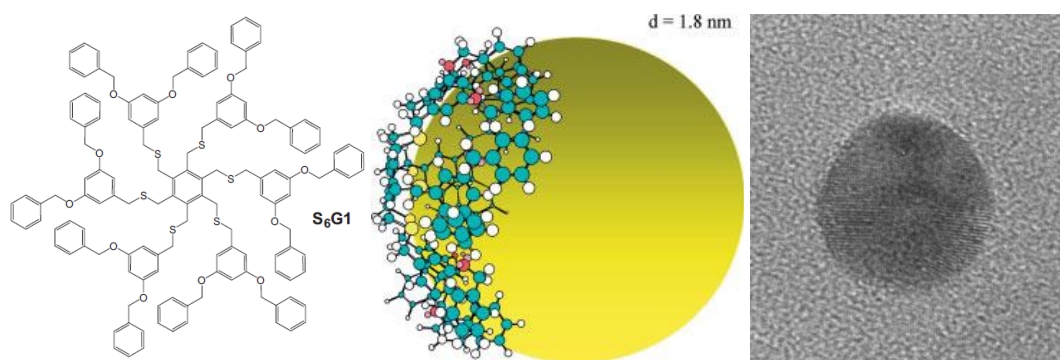


Figure 26 – On the left: S₆G1 structure of Oligothia-type dendrimer used as a capping agent for AuNPs, the schematic representation on AuNP is presented (in the middle) and HR-TEM image showing 1.8 nm particle capped by S₆G1 (on the right). Taken and adapted from D’Aléo *et al.*^[20]

Luisa De Cola introduced Oligothia dendrimers as templates for the formation of AuNPs. These dendritic sulfur-containing structures, according to their generation, led to different size and stabilization of the particles (**Figure 26**). The kind of stabilization involved is compared to that obtained with alkanethiols with the advantage of the smaller thickness of the shell around the particles.^[20]

Kim *et al.* reported the preparation of nearly size-monodispersed AuNPs in a PAMAM dendrimer template-based approach to form DENs^[21] that can be extracted with the introduction of *n*-alkanethiols.^[9] Particles in the size range of 1–2 nm are accessible and the very low size distribution of 0.3 nm is reported. Magic numbers of equivalent ratios of AuCl₄[−]/dendrimers are invoked (e.g., [HAuCl₄]:[G*n*-Q*p*] = 100) to explain these surprising results whereas various sizes and large size distributions were usually observed.^[1-8]

First to third generation lysine-based disulfide dendrimers were used as stabilizers to form AuNPs according to Brust’s two-phase protocol as reported by Chechik and co-workers.^[22] Interestingly the size of the resultant particles was found to decrease with the

increasing dendrimer generation and the opposite behavior was observed when increasing the temperature during the synthesis.

Crooks *et al.* presented G4-PAMAM dendrimer modified on its periphery with dodecyl groups allowing the formation of DENs in organic solvents, toluene in this case.^[23]

A first-generation Fréchet-type thiol-terminated dendron was used in different mole ratios of dendrimer to gold to produce AuNPs: the size was found to increase when the ratio decreased.^[24] DSC study showed that the G1-dendron assembled onto AuNPs did not show the phase transition exhibited when analyzed as a free ligand.

Poly(benzyl ether) alcohol dendrons (G_n -OH, $n = 1-3$) have been used as a stabilizing medium in the preparation of gold nanoparticles. The G_n -Au nanoparticle composites are stable and resist aggregation at room temperature.^[25] Apparently, under the same reaction conditions (same ratios between HAuCl_4 , NaBH_4 and G_n -OH), the particle size increases with increasing generation. This result has to be compared to Chechik's results^[22] presenting the opposite behavior. He concluded that the nature of the dendritic system must play an important role in determining the characteristics of the gold core. The size relationship can be explained in terms of steric effects as the much more bulky, third generation dendritic system would be expected to pack more efficiently around a small core with a high curvature surface, hence favoring a smaller particle size. The first generation ligands can pack together more easily favoring the formation of larger nanoparticles with a 'flatter' surface.^[22]

A dendrimer containing a carboxylic acid core, a rigid biphenyl group, and three perfluorinated tails served as a supramolecular template to form AuNPs after reduction of Au(III) with UV irradiation. A well-ordered supramolecular assembly was subsequently observed in this case.^[26]

First to second generation Newkome-type dendrons (dendritic disulfide ligands) were used to stabilize AuNPs *via* the Brust's monophasic method. As results Chechik and co-workers^[27] noticed the role of dendrons on nanoparticles sizes: the nondendritic ligand generates ill-defined NP, while dendritic ligands clearly exert significant control over the particle growth process giving rise to gold cores which are not only smaller but have much narrower size distributions. They also note that with theses Newkome-type dendrons increasing the dendritic generation did not result in decreasing the gold core size as reported for Lysin-based dendrons earlier^[22] and other groups' results.^[18, 28-30]

Chechik discussed about 1) the dendritic effect of branching with the conclusion that larger dendrons were less effective at stabilizing the NPs because they were less packed consequently more subjected to etching, and 2) the effect of the dendritic structure where hydrogen bonds possibly formed within the dendrons would lead to the ‘grouping together’ and hence leave gaps leading to less stable particles.^[27] In addition they noticed from their studies^[22, 27] that dendrimers with higher symmetry lead to more stable AuNPs most probably because of a more efficient packing of the dendrons on the surface.

G₂ poly(benzyl ether) hydroxyl-functionalized dendrons were found capable of stabilizing AuNPs.^[31] However the result reported by Jiang *et al.* lead to a relatively wide size distribution of these NCDs probably because of the weak stabilization of the hydroxyl groups.

Shon and Choi presented a concise review of synthetic strategies for NCDs from metal NPs, with an emphasis on their current applications.^[32] The synthesis of nanoparticle-cored dendrimers represents an important advance to the control and preparation of new organized nanostructures. The most popular way for the synthesis of nanoparticle-cored dendrimers is a direct method using a modified Schiffrin reaction with dendrons containing thiol or disulfide groups. The second method is an indirect method involving two-step reactions, the synthesis of monolayer-stabilized nanoparticles followed by the ligand-place exchange with thiolated dendrons. Thirdly, a new synthetic strategy to build dendritic architectures around a monolayer-protected nanoparticle using single or multi-step organic reactions is described. Two different approaches for this new synthetic method are attempted. Convergent approach is based on a strategy in which the synthesis of monolayer-protected nanoparticles is followed by adding dendrons on nanoparticles by a single coupling reaction. Divergent approach uses multi-step reactions to build dendritic architectures around a nanoparticle core.

Ravoo highlighted dendrimers as versatile building blocks for “bottom-up” nanofabrication because they combine molecular structure and nanoscale dimensions. Moreover, dendrimers can be functionalized at their numerous peripheral end groups, in their core, along their branches, and in the voids of their interior. This frontier brings out the potential of metal containing dendrimers for nanofabrication.^[33]

Dendrimer/AuNPs systems have applications for cancer-cell targeting and imaging for example.^[34]

3.2. Esterification between dendrimers and AuNPs

3.2.1. About esterification

The use of dicyclohexylcarbodiimide (DCC) as a promoter represents one of the most versatile esterification methods (**Figure 27**). Although this reagent is irritant to skin and a stoichiometric dosage or more is necessary, this procedure enjoys various advantages. The reaction usually proceeds at room temperature, and the reaction conditions are so mild that substrates with various functional groups can be employed. The reaction is not sensitive to the steric bulk of the reactants, allowing production of esters of tertiary alcohols. As such a wide range of applications has been achieved in the fields of natural products, peptides, nucleotides, etc.^[35] Alternatively to DCC, *N,N'*-diisopropylcarbodiimide (DIPC) can be used as both of them have greater stability and availability compared to other carbodiimides that either decompose or polymerize. Moreover DIPC is liquid at room temperature which makes it easier to handle.

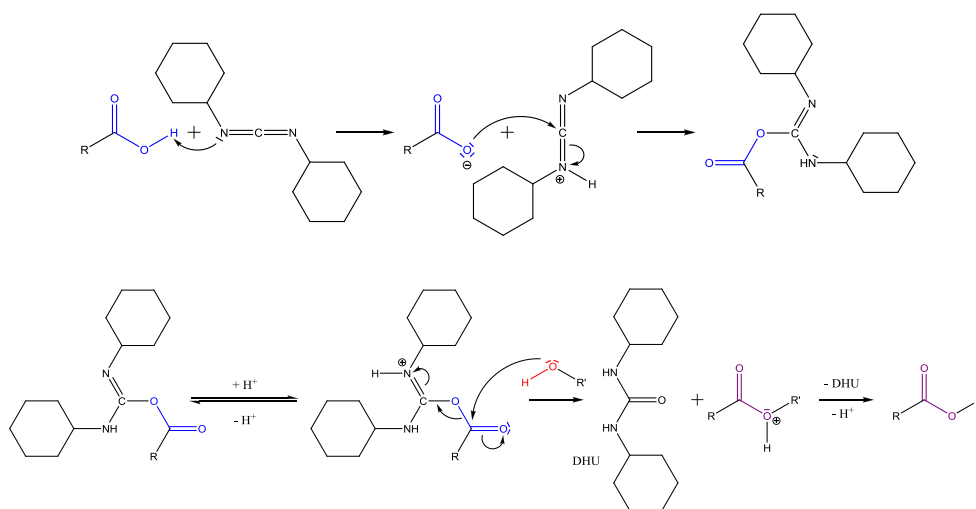


Figure 27 – Carbodiimide DCC is used as an activator able to form an *O*-acylisourea intermediate, which offers reactivity similar to the corresponding carboxylic acid anhydride. The alcohol may be added to the activated carboxylic acid to form the stable dicyclohexylurea (DHU) and the ester.

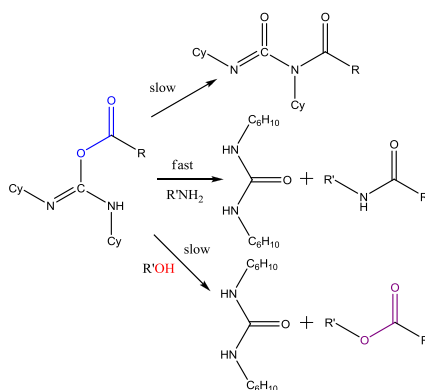


Figure 28 – *N*-Acylureas, which may be quantitatively isolated in the absence of any nucleophile, are the side products of an acyl migration that takes place slowly. Strong nucleophiles such as amines react readily with the *O*-acylisourea and therefore need no additives.

The DCC method in pure organic synthesis, however, unfortunately suffers from some drawbacks: yields are not always high, undesirable *N*-acylureas are occasionally formed and reactions with alcohols are relatively slow (see **Figure 28**). These drawbacks can be overcome by addition of catalytic amounts of *p*-aminopyridines. Thus the original procedure was refined by Steglich by adding 4-(*N,N*-dimethylamino)pyridine (DMAP) as a catalyst to improve the variable yields, satisfactory only in the case of phenols and thiophenols.^[36] The mechanism for the reaction is suggested in **Figure 29**.

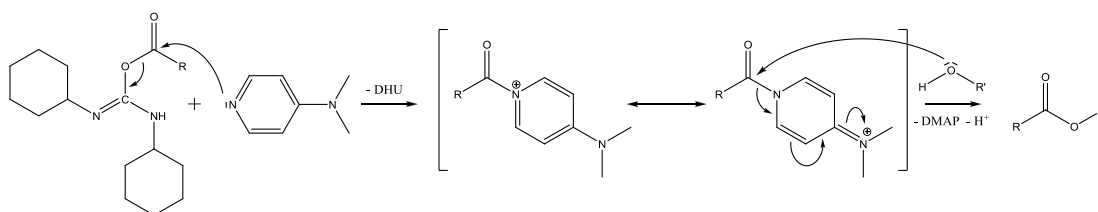


Figure 29 – A common explanation of the DMAP acceleration suggests that DMAP, as a stronger nucleophile than the alcohol, reacts with the *O*-acylisourea leading to a reactive amide ("active ester"). This intermediate cannot form intramolecular side products but reacts rapidly with alcohols. DMAP acts as an acyl transfer reagent in this way, and subsequent reaction with the alcohol gives the ester.

In practice, the reaction with carboxylic acids, DCC and amines leads to amides without problems, while the addition of approximately 5 mol-% DMAP is crucial for the efficient formation of esters.^[35, 36]

As results,^[36] methyl or *p*-nitrophenyl esters of pivalic and 2,4,6-trimethylbenzoic acids are obtainable. *tert*-Butyl esters of 3,5-dinitrobenzoic acid and glycerol tristearate can also be prepared: these esters are not accessible without the use of *p*-aminopyridines. However, combinations of *tert*-butyl alcohol and more sterically demanding acids such as

adamantanecarboxylic acid or 1-phenyl-cyclohexane-1-carboxylic acid fail to afford the desired esters. The mechanism of the catalyzed reaction is depicted in **Figure 30**.

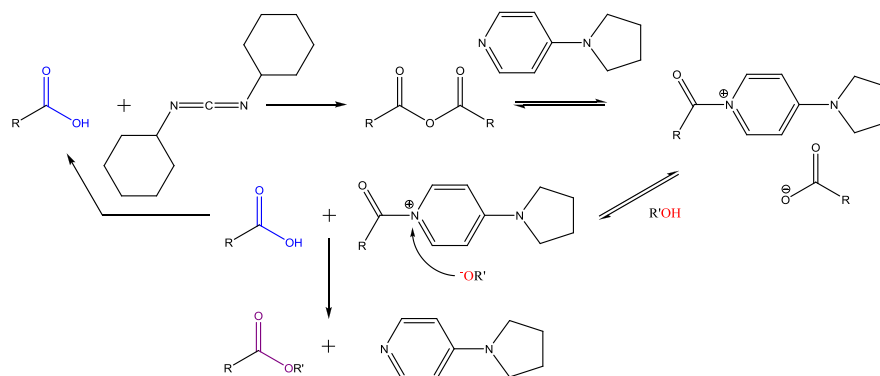


Figure 30 – The carboxylic acid is first converted by DCC into an anhydride, which then forms an acylpyridinium species with *p*-aminopyridine (here 4-pyrrolidinopyridine). Nucleophilic attack on the acyl group by $R'O^-$ produces the ester concomitantly with regeneration of *p*-aminopyridine, together with a half quantity of $RCOOH$ which is again subjected to the reaction with DCC.

Brønsted acids such as *p*-toluenesulfonate (*p*TSA) allow a convenient transesterification when used in catalytic amounts. However it was shown that the use of an equimolar mixture of *p*TSA and DMAP lead to the formation of 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) which suppress the side reaction leading to the formation of *N*-acylurea.^[37]

Back to our case, the use of these conditions appeared necessary as the hydroxyl-functionalized particles we synthesized were soluble in organic solvents and the dendrimers bearing carboxylic acids involved in the esterification reaction were generally quite bulky leading to low yields or no coupling reaction under other reaction conditions.

3.2.2. AuNPs and esterification

Nanoparticle-cored dendrimers (NCDs) were recently synthesized by the reduction of metal precursors in the presence of dendronized thiols or disulfides.^[18, 19, 28, 38] However, this approach is somewhat problematic because it requires a large excess of dendronized thiols or disulfides, especially for the synthesis of NCDs with a small and monodispersed nanoparticle core. This approach also provides little control over the nanoparticle-core dimension.^[7-10] A more convenient and cost efficient synthetic methodology for the synthesis of NCDs with controlled particle core size, generation, and dendritic wedge

density is highly desired for the basic understanding of the relationship between structure and properties of these new class of hybrid nanostructures.

Particles can be esterified to attach AuNPs to substrates and to other AuNPs through a covalent network of ester bonds.^[39]

Since the reaction only takes place at the exterior of monolayer-protected gold nanoparticles, this approach can maintain an intact core size for the synthesis of NCDs with different interior layers (generations) and dendritic wedge densities.

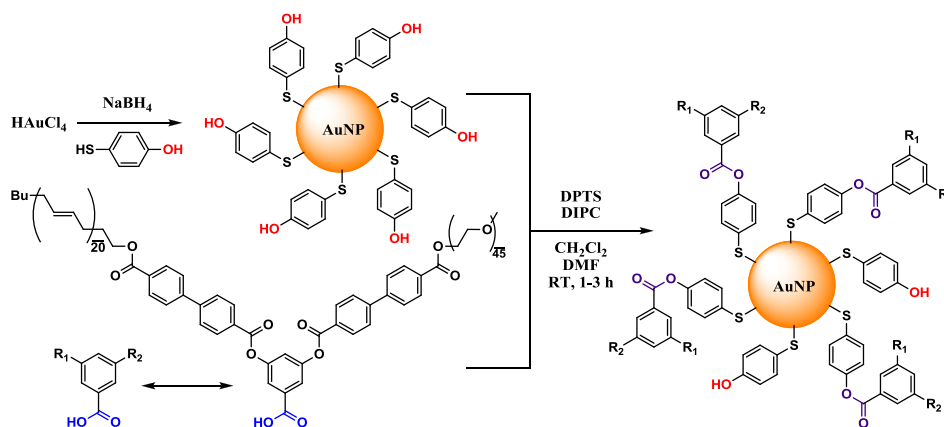


Figure 31 – Synthesis pathway reported by Zubarev *et al.* leading about 65% of amphiphile esterified on hydroxyl-terminated AuNPs (adapted from Zabarev *et al.*^[40]).

Zubarev and co-workers reported the synthesis of amphiphilic gold nanoparticles with V-shaped arms.^[40] Basically, hydroxyl-terminated AuNPs are first synthesized and in parallel, a polybutadiene-poly(ethylene glycol) amphiphile bearing a carboxyl is synthesized. Then, in the presence of 1,3-diisopropylcarbodiimide (DIPC) and 4-(*N,N*-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) both the particles and the amphiphile are coupled in dichloromethane by esterification reaction (**Figure 31**). According to the conditions used it was calculated that about 65% of the initial hydroxyl groups on AuNPs were esterified within the first 2 h.

Butanethiol-protected AuNPs were subjected to a place exchange reaction with 6-mercaptohexanoic acid followed by a covalent coupling as an amide bond between the carboxyl from the particles and amines from a 5th generation PAMAM dendrimers.^[41]

Young Shon and co-workers reported the dendritic functionalization of AuNPs.^[42] 11-Mercaptoundecanoic acid/hexanethiolate-protected gold clusters were synthesized according to Brust's method followed by the ligand place-exchange reaction. A

convergent approach for the synthesis of nanoparticle-cored dendrimers uses a single step reaction that is an ester coupling reaction of hydroxyl-functionalized dendrons with carboxylic acid-functionalized gold clusters. A divergent approach, which is based on multi-step reactions, employs the repetition of an amide coupling reaction and a Michael addition reaction to build PAMAM dendritic architectures around a nanoparticle core.

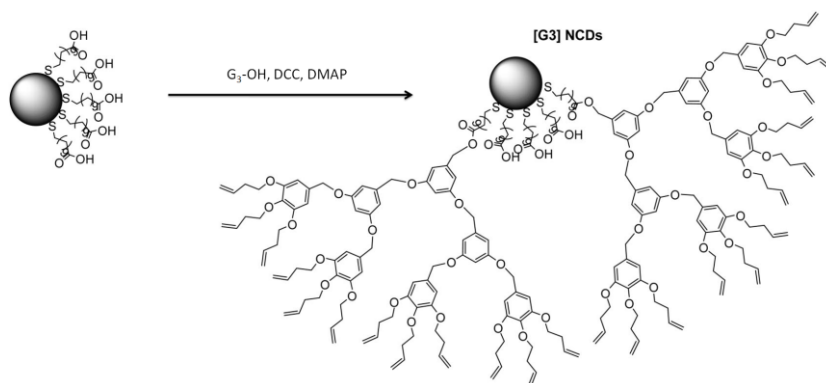


Figure 32 – Synthesis of G₃ NCDs by the ester coupling reaction leading to about 10% of dendrons on AuNPs surface. Adapted from Shon and Choi.^[43]

Shon *et al.* reported the convergent dendritic functionalization of AuNPs by an esterification.^[43] Prior to the coupling reaction, AuNPs were synthesized having various loadings of carboxyl groups, the latter being introduced *via* a place exchange reaction on hexanethiol-stabilized AuNPs with 11-mercaptoundecanoic acid (MUA). The resulting MUA AuNPs can exhibit more or less carboxyl groups through the control of the volume of the incoming MUA in the exchange reaction. These AuNPs are subsequently treated with DCC and DMAP in THF to tether 10% of G₁ up to G₃-OH dendrons (**Figure 32**).

Alternatively AuNPs can be functionalized through different techniques such as 1,3-dipolar cycloaddition reactions – click chemistry – providing an interesting alternative to the esterification reaction.^[44]

3.3. AuNPs and LC dendrimers

3.3.1. AuNPs and LC dendrimers mixtures

Except for the use of LC phases as templates and matrices for AuNP synthesis, the combination between NPs and LC let glimpse the possibility of new hybrid materials for optical and electro-optical applications. One of the main inconvenient of these mixtures is their long-term stability. Indeed NPs often aggregate after a short period in spite of the LC host surrounding them. The latter is supposed to ensure solubility and miscibility. Some selected examples of strategies which were adopted to address these problems in the case of these mixtures are presented.

In a recent review, Hegmann highlighted the particular role liquid crystalline materials play in the synthesis and preparation of size and shape-uniform nanostructures, the use of condensed liquid crystal phases for nanoparticle assembly. The interactions between nanomaterials and liquid crystal phases leads to unique defect structures or to new and exciting properties for the use of this materials combination in high-tech applications.^[45]

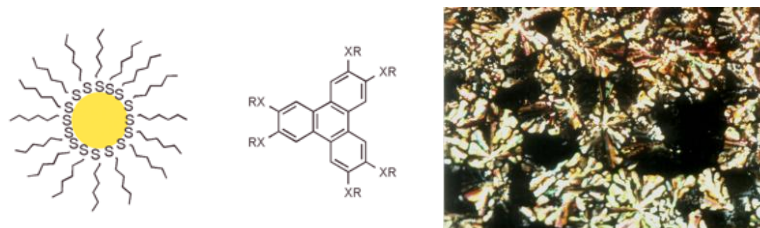


Figure 33 – Left: hexanethiolate-capped AuNPs mixed with hexahexylthiotriphenylene (i.e. $RX = C_6H_{13}S$) (in the middle); Right: Columnar phase observed by POM at 80 °C corresponding to a mixture of 1:3 weight ratio AuNPs-LC. Taken from Kumar and Lakshminarayanan.^[46]

Kumar reported the thermophysical properties of mixtures of hexanethiolate capped gold nanoparticles and three types of discotic liquid crystals, investigated using POM, DSC and conductivity measurements, indicate inclusion of AuNPs into a matrix of triphenyl-based discotic liquid crystals (see **Figure 33**).^[46, 47] While a minor shift in the transition temperatures between mesophases was observed, the isotropic temperature decreases when the amount of AuNPs increases and in addition the nature of the mesophases is not altered in these composites.

Obtaining LC-functionalized AuNPs would not be possible without the synthesis of suitable LC ligands including in particular a thiol function allowing a strong connection to the gold and consequently more stable compounds. Thus Kumar *et al.* reported the synthesis of thiol-functionalized alkoxy cyanobiphenyl with various alkane chain lengths.^[48] All compounds exhibit a nematic phase and variations in the alkane chain length modify the glass transition temperature as well as the nematic-to-isotropic transition temperature (increase during heating and decrease during cooling).

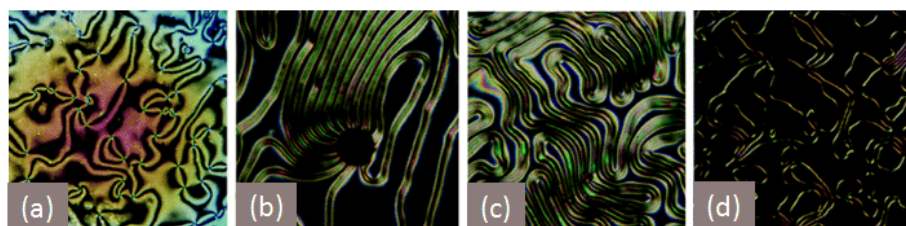


Figure 34 - POM micrographs (crossed polarizers) of the N phase taken on cooling from just below the I–N phase transition: (a) schlieren texture of phenylpyrimidine derivative LC1 (68 °C); (b) stripe texture of the N phase of 5 wt% C₁₂H₂₅–SH-capped AuNPs (Au2) in LC1 (64 °C); stripe texture and coexisting areas with homeotropic alignment: (c) 5 wt% Au2 in LC1 (61 °C); (d) stripe pattern of the N phase of 5 wt% Au2 in LC1 in rubbed polyimide ITO glass cell (cell gap: 5 mm, no electric field applied). Taken from Qi and Hegmann.^[49]

Qi and Hegmann reported the mixtures of nematic liquid crystals (N-LC, 5-heptyl-2-(4-(octyloxy)phenyl)pyrimidine) with C₆H₁₃–SH- and C₁₂H₂₅–SH-capped AuNPs (2.1 ± 0.6 nm and 7.4 ± 2.3 nm respectively).^[49] All AuNPs–LC mixtures show strikingly similar textural characteristics between untreated glass slides as well as in cells coated with polyimide alignment layers. On cooling from the isotropic liquid phase, patterns of birefringent stripes occur separated by areas of homeotropic alignment despite surfaces commonly promoting parallel alignment of N-LC molecules (**Figure 34**). While the specific combination of the gold nanoclusters and the used N-LCs produces significant changes in the topological (defects, dipoles, and chain-like particle aggregates) and rheological properties (qualitatively increased viscosity), other properties such as phase transition temperatures and phase stability are only mildly affected (I–N phase transition temperatures decrease of 1–2 °C), and the phase transitions remain sharp, as was observed earlier by Kumar *et al.*^[46, 47] The specific interactions between the N-LCs and the gold colloids, the formation of topological defects, homeotropic anchoring of the LC molecules to the colloid surface, and the elastic properties of the N-LC all play integral

roles in the spontaneous assembly of the gold nanoparticles into chain-like aggregates similar to other quasi-spherical particles.

Qi *et al.* demonstrated an alignment and switching mechanism in planar LC cells using N-LC molecules with positive value of dielectric anisotropy and small amounts of alkyl thiolate-capped AuNPs. The threshold voltages were lower and the dielectric constants were higher than the values obtained for the pure N-LCs.^[50]

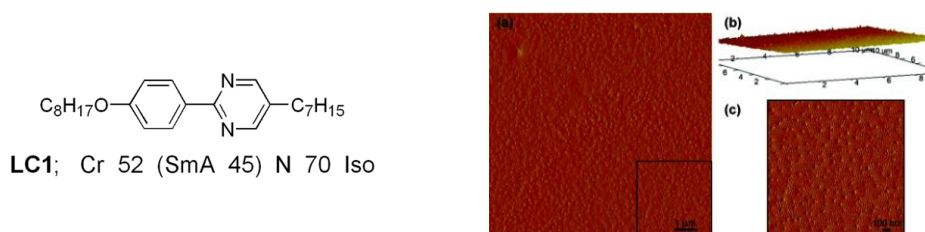


Figure 35 – Left: chemical structure and LC mesomorphism including phase transition temperatures (°C) of LC1; Right: tapping mode AFM image of a 5 wt % C₆H₁₃-SH AuNPs in LC1 suspension after spin-coating and drying: (a) amplitude, (b) 3D (height profile), and (c) magnified section of image a. One can see an almost even distribution of the AuNPs on the surface which is characterized by small, almost spherical protrusions (~20–25 nm in diameter and height) that are attributed to either individual or small assemblies of Au NPs covered by the nematic LC. Taken from Qi and Hegmann.^[51]

Qi and Hegmann have shown that the alignment of nematic LCs can be tuned by doping them with alkyl thiolate-capped Au NPs (1.6 nm C₆H₁₃-SH AuNPs, 1.9 and 5.4 nm C₁₂H₂₅-SH AuNPs). The temperature- and concentration-dependent, and in some cases rather sudden change of the LC alignment is governed by the different solubility of the Au NPs initially in the isotropic phase, but also in the nematic phase itself. Hence, the alignment of the NP-doped nematics significantly depends on the order parameter (i.e., on the temperature) and ordering either in the bulk or around the NPs residing at the interface, the concentration, and on the sample preparation conditions (**Figure 35**). In principle, all phenomena discussed by Qi and Hegmann reflect the level of “incompatibility” of certain AuNPs in nematic LC hosts. Ideally, functionalized AuNPs require a minimum solubility in the LC host to prevent aggregation, yet a certain incompatibility (depending on the above-mentioned parameters) is critical to induce the described alignment effects. Qi and Hegmann were not able to show if decorating metal NPs with nematic molecules would improve the usefulness of NPs as alignment materials for LCDs because recent results showed that conventional miscibility rules between LC hosts and organic dopants do not strictly apply to NP-doped nematic mixtures.^[52]

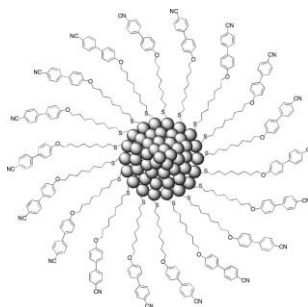


Figure 36 – AuNPs capped with 4'-(8-mercaptooctyloxy)-4-biphenylcarbonitrile (8OCB-SH) intended to be used in LC 'solvent' having the same cyanobiphenyl moieties. Taken from Goodby *et al.*^[53]

However Goodby *et al.* reported AuNPs coated with mesogenic thiols and studied the behavior of doped nematic, smectic, and cholesteric phases, from compounds such as the one presented in **Figure 36**. In particular, the stabilizing mesogenic cyanobiphenyl-terminated thiols chosen^[48] were designed to match perfectly the chemical nature of the liquid-crystal solvent to be used to increase solubility and avoid the possibility of separation as a result of chemical incompatibility of the particle and solvent. These nanoparticles are found highly soluble in the liquid-crystal solvents studied without the need of sonication, giving dark brown solutions. They show complex thermal behavior near to the nematic to isotropic liquid transition, but in the present case the particles are of similar size as the liquid-crystal solvent molecules.

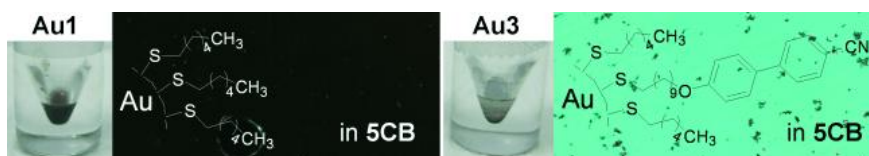


Figure 37 – V-vials containing 5CB doped with AuNPs and corresponding POM images (uncrossed polarizers). 5 wt % of AuNPs were mixed to 5CB LC: the C_6H_{13} -SH-capped AuNPs (Au1)/5CB mixture is homogeneous whereas AuNPs including 10OCB (Au3), to match the chemical nature of the LC solvent, in 5CB LC aggregate after a while. Taken from Qi *et al.*^[52]

Hegmann and co-workers have synthesized AuNPs coated by C_6H_{13} -SH on the one hand and $C_{12}H_{25}$ -SH on the other hand. After a place-exchange reaction on the latter they obtained mixed layers of alkanethiol and 4'-(10-mercaptodecyloxy)-4-biphenylcarbonitrile (HS10OCB). Then they subjected both the AuNPs with or without LC ligand in their shell and, quite surprisingly, it appeared that the structurally related CB end-capped gold NPs were less compatible (less miscible/dispersible) in comparison to NPs homogeneously covered “only” with alkanethiols of different chain lengths (see

Figure 37 for illustrative example). At least for the systems they presented, maybe for all polar nematics, or eventually also for many other LC/nanomaterial combinations, they noticed that common concepts of solubility and miscibility between two components in LC mixtures do not strictly apply. Decorating NPs with functional molecules such as polar aromatics poses the risk of increasing self-attraction through van der Waals forces, π - π stacking and/or dipole-dipole interactions in addition to the attractive forces already active between NPs (predominantly between metallic, magnetic and ferroelectric NPs). Unfortunately electro-optic tests did not hint at any significant difference between partly LC and non-LC decorated NPs.^[52]

3.3.2. LC-dendrimer-tethered AuNPs

Chuard *et al.*, Dardel *et al.*,^[54-56] and Deschenaux *et al.*^[57] reported the LC functionalization of fullerenes, the supramolecular organization of which can be controlled by liquid-crystalline dendrimers. These LC-capped non-mesomorphic units can exhibit smectic, chiral nematic or columnar phases. One should notice the similarity of shape between spherical particles and C₆₀ fullerenes thus it seems interesting to extend the concept of fullerene-cored dendrimers to the one of nanoparticles-cored dendrimers. The LC moieties should transfer to the gold system but taking into account the weight of a C₆₀ fullerene in relation to the one of a AuNP of comparable diameter, that is 0.72 compared to 7.96 kg/mol, i.e. an elevenfold mass has to be encapsulated and organized by dendrimers. However, the following recent examples illustrate the possibility of implementing such systems.

The functionalization of gold nanoparticles with liquid crystalline moieties is a rather new field of research. To the best of our knowledge the first report on that subject (AuNPs and LC dendrimers) dates back to 2001 where Ikeda and co-workers reported the successful preparation of 3-nm AuNPs covered by a liquid-crystalline thiol-derivative by Brust's biphasic method (**Figure 38**, left), the purity of which is confirmed by ¹H NMR (**Figure 38**, middle).^[58]

The final material was presented as AuNPs having a core of 920 gold atoms and 270 LC ligands lying on the 320 Au atoms of the surrounding AuNP layer: thus the coverage reach a value of $\gamma = 0.84$ which is high when usual value are between 0.6 and 0.7 and

equals 0.66 for $C_{12}H_{25}$ -SH alkane chains.^[59] According to this ligand geometry, a more efficient packing should not be expected.¹

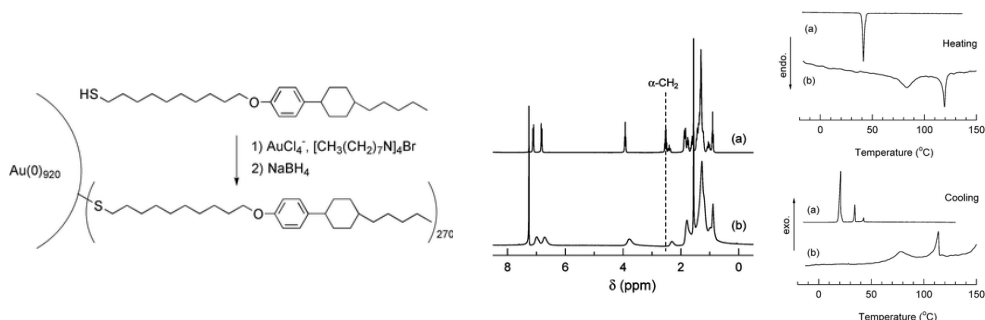


Figure 38 – AuNPs were synthesized using a mesogenic compound (4'-(10-mercaptooctyloxy)-4-pentylcyclohexyl)benzene) as stabilizing agent according to Brust's biphasic method (on the left). The purity of the final material is confirmed by ^1H -NMR spectroscopy asserted by the absence of the $\alpha\text{-CH}_2$ signal of ligands on AuNPs in spectrum (b) (in the middle). DSC thermograms of (a) ligand and (b) AuNPs (on the right). Taken from Kanayama *et al.*^[58]

The free ligand exhibits a nematic and a smectic phase on cooling (between 43-34 °C and 34-21 °C respectively) whereas the thermal behavior of AuNPs is quite different: the functionalized system shows an enantiotropic LC behavior between 77 and 100 °C (**Figure 38**, right) but no mesophase was identified.

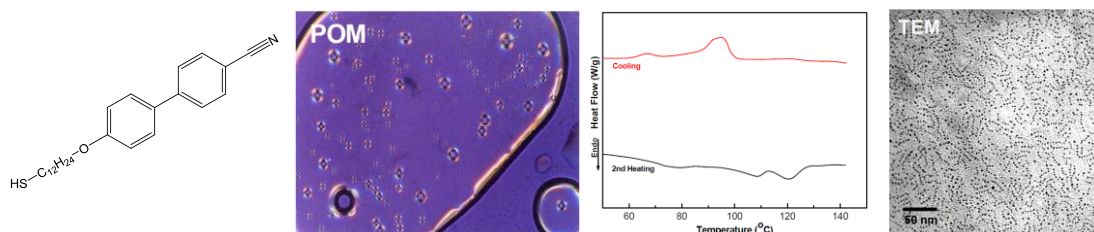


Figure 39 – Left: Structure of the LC cyanobiphenyl thiol ligand (LC-SH); Middle: POM of the mesophase obtained for the free LC-SH ligand at 60°C; Right: DSC curve and TEM image of AuNPs after thermal treatment (140 °C for 3 h followed by 125 °C during 4 h). Taken from Ref.^[60]

Following this first communication, a second one appeared in 2004 where a liquid-crystalline thiol ligand, namely 4'-(12-mercaptododecyloxy)biphenyl-4-carbonitrile, was successfully synthesized and used for the formation of AuNPs, with the size 2.7 ± 0.5 nm

¹ After recalculations it was found that the correct estimation formulae are $\text{Au}_{820}\text{L}_{225}$ ($\gamma = 0.70$ with $\chi_{\text{org}} = \%C + \%H + \%S$) and $\text{Au}_{820}\text{L}_{196}$ ($\gamma = 0.61 = \chi_{\text{org}} = 1 - \%Au$), the latter being less correct due to the uncertainty about the gold percentage from elemental analyses because size distribution was not specified in the communication from Ikeda and co-workers.

(see **Figure 39**).^[60] Moreover the particles formed exhibit a one-dimensional arrangement (see chapter 1.1 for a description). The LC thiol ligand showed a nematic phase between 50 and 66 °C – from DSC and POM analyses – and the corresponding LC-capped AuNPs revealed an unidentified mesophase between 110 and 130 °C (shown in **Figure 39**).

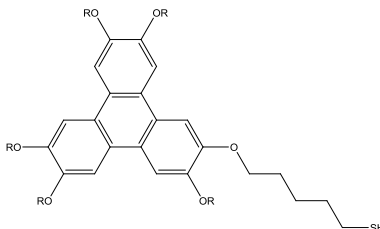


Figure 40 – Monothiol-functionalized triphenylene derivative used in a place exchange reaction on hexanethiolate-capped AuNPs (here R = C₅H₁₁). Taken from Kumar *et al.*^[47]

After the mixture of LC triphenylene derivatives with C₆H₁₃-SH-capped AuNPs (see § 3.3.1), Kumar reported the place exchange reaction of the latter with a triphenylene thiol derivative (**Figure 40**) in a 1:1 ratio in the final material (determined by ¹H NMR).^[47] Unfortunately they do not comment on the properties of LC-functionalized AuNPs compared to the simple mixture of the two.

Park and Stroud showed that, when a AuNP is coated by a thin layer of nematic liquid crystal, the nanoparticle surface has a strong effect on the director orientation, but, surprisingly, this deformation can enhance the surface plasmon splitting. They consider three plausible liquid crystal director configurations in zero electric field: boojum pair (north-south pole configuration), baseball (tetrahedral), and homogeneous. From the discrete dipole approximation, they find that the surface plasmon splitting is largest for the boojum pair, and this result is in good agreement with experiment.^[61] They conclude that there is a wide range of applications in nanoscience and nanotechnology, because they show that optical properties of systems containing nanoparticles can be sensitively controlled with the use of liquid crystals. The transmission and absorption of such materials could be tuned by a dc electric field, which will alter the liquid crystal director field, or by controlling the surface interactions between metal and liquid crystal.

Yamada *et al.* reported the synthesis of AuNPs fully coated with discotic liquid crystalline molecules of hexaalkoxy-substituted triphenylene (Au-TP).^[62] Controlling the molar ratio of TP disulfide (TPD) allows one to influence the mean diameter of Au-TP:

decreasing the ratio increases the size of particles; in addition the size dispersion remains quite low in the range 0.3-0.4 nm.

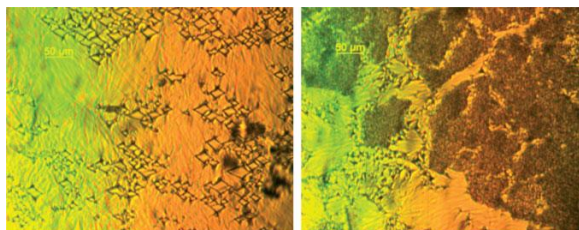


Figure 41 – Left: LC texture of a mixture of 5CB and a chiral dopant (cholesteryl oleyl carbonate, COC); Right: in the same LC mixture but doped by 3.4 wt % of NPs, disclination of focal conics as well as dark regions can be noticed. Taken from Worden *et al.*^[63]

With a view to mix them with LC phases, many groups tethered LC moieties onto AuNPs. The two main approaches are on the one hand the direct synthesis with mesogenic thiol derivatives or alternatively ligand exchange reaction with thiolated mesogens. Most of them were presented in the last part (see 3.3.1): Goodby,^[53] Miyake,^[62, 64] and Hegmann,^[50-52, 65] used calamitic or discotic mesogens. Yet another approach is the one that does not consist in considering the NPs among LC host as impurities that disrupt the LC order by preventing them to align correctly (**Figure 41**),^[63] but as independent units such as DENs or NCDs capable of inducing the 1D and 2D order in dispersed particles on the colloidal scale.

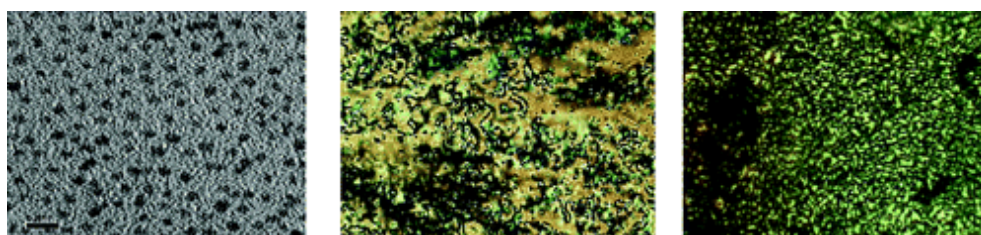


Figure 42 – Left: TEM picture of hexylthiol-covered AuNPs subjected to ligand exchange with thiolated laterally-branched mesogens (scale bar 5 nm); Middle: POM image of the thiolated laterally-branched mesogen; Right: POM image of AuNPs including the mesogens in their shell. Taken from Cseh and Mehl.^[66]

Cseh and Mehl have prepared novel nematic gold nanoparticles, where the spherical particles are covered with a monolayer of laterally-branched mesogens and short hydrocarbon chains. The materials are chemically stable and exhibit nematic phase behavior at room temperature (**Figure 42**).^[66] They noticed that a variation in the particles

size and the hydrocarbon chain length modifies the onset and the range of the liquid crystal phase.^[67]

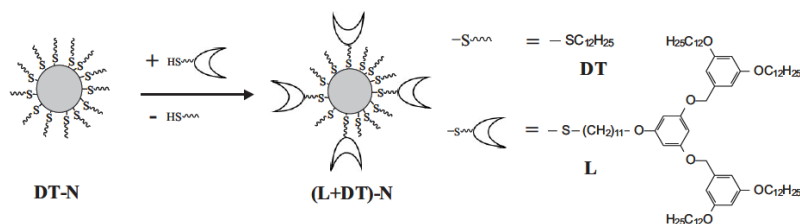


Figure 43 – Schematic representation of the nanoparticle exchange reaction yielding mixed dodecanethiol- and 2nd generation dendritic ligand-capped AuNPs ((L+DT)-N) and chemical structure of the surface-protecting groups (dodecanethiol **DT** and G₂ dendritic ligand **L**) used by Donnio *et al.* Taken from Donnio *et al.*^[68]

Donnio *et al.* reported AuNPs possessing a positionally ordered 3D liquid crystalline phase in the bulk.^[68] They are made from dodecanethiol-capped AuNPs which were then subjected to thiolated G₂ dendrons during a place exchange reaction (**Figure 43**). Induction of the mesophase results from the synergy between the gold core and the non-mesogenic dendrons. These particles also exhibit ferromagnetic behavior up to 400 K and are able to self-organize in a 2D hexagonal array on solid substrates.

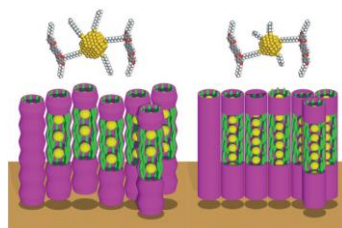
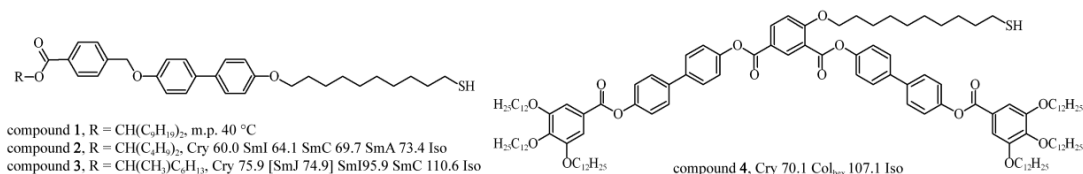


Figure 44 - Schematic models of the gold string structures reported by Zeng *et al.* It was found that the unit cell belonging to one nanoparticle is 45% shorter in the column direction but only 11% narrower laterally in the hexagonal *p6mm* columnar phase for AuNPs AuL4C6 (mesogenic and hexanethiol ligands, above right) compared to the rhombohedral *R3m* phase in AuNPs AuL4C12 (mesogens and dodecanethiol ligands, above left). Taken from Zeng *et al.*^[69]

Ungar and co-workers reported AuNPs covered with a nematic liquid-crystal ligand laterally attached *via* a thioalkyl spacer and a thioalkane “diluent” and that exhibit 3D ordering in strings jacketed by the mesogens with controllable interparticle spacing (between 4 and 16 Å) *via* the combination of the spherical and rod-like moieties. The particles form rhombohedral and columnar superlattices (hexagonal and rectangular), which is not the usual packing modes of spheres.^[69] Moreover the nematogenic ligand

was found as the only possible source of biaxiality confirmed by the Bragg diffraction from the rectangular lattice in the AuNPs including hexanethiols, as neither the AuNPs nor the molten alkyls have the required low symmetry.

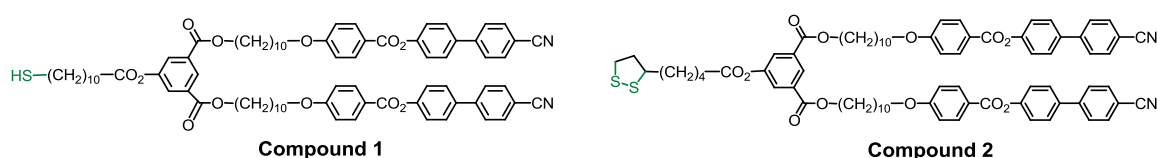


Scheme 7 - Molecular structure and phase properties of mesogenic thiols used by Wojcik *et al.* for grafting to gold clusters.^[70] Cry=crystalline, Sm=smectic, Iso=isotropic, Col_{hex}=columnar hexagonal.

Wojcik *et al.* reported the spontaneous formation of smectic and columnar structures that were observed when spherical AuNPs were functionalized with mesogenic thiols (**Scheme 7**). The particle ordering is stimulated by softening of the interparticle potential and flexibility for deformation of the grafting layer.^[70]

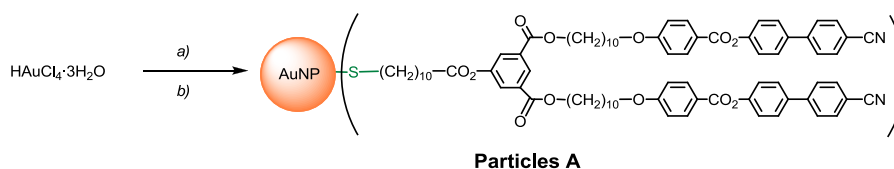
3.4. Results and discussion

3.4.1. Direct synthesis and ligand exchange

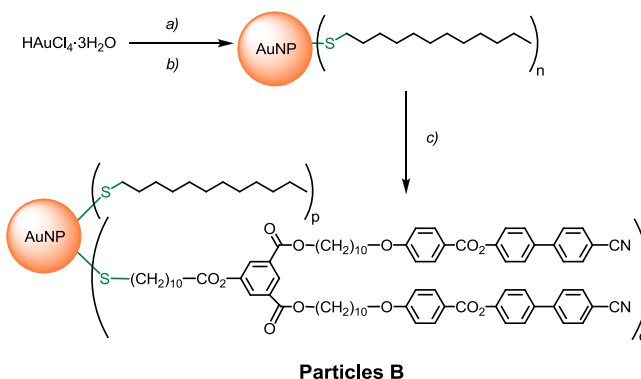


Scheme 8 – First-generation dendrons bearing a thiol or disulfide function allowing them to carry out a direct synthesis or a place exchange reaction.

First-generation poly(aryl ester) dendrons functionalized with mesomorphic cyanobiphenyl units and containing either a thiol or a disulfide group (compounds **1** and **2** in **Scheme 8** respectively) were synthesized.^[71] The disulfide function (two anchor sites) was selected to design ligands having a stronger binding constant than the thiol derivatives (one anchor site). Mesomorphic properties and characteristics of compounds **1** and **2** are presented in the Second appendix.



Scheme 9 – *a*) Tetraoctylammonium bromide (TOAB), toluene/water (4:1), RT, a few min; *b*) compound **1**, 30 min, then NaBH₄, toluene, RT, inert atmosphere, 24 h, 3%.



Scheme 10 - *a*) TOAB, toluene/water (4:1), RT, a few min; *b*) 1-dodecanethiol, 30 min, then NaBH₄, toluene, RT, 1 h, 30%; *c*) compound **1**, CH₂Cl₂, RT, inert atmosphere, 72 h, 50%.

The functionalization of gold nanoparticles was achieved by two alternative protocols: 1) the direct synthesis,^[72, 73] (**Scheme 9**) and 2) the ligand exchange reaction^[74, 75] (**Scheme 10**). From the point of view of functionalization, the direct method leads to full coverage of the nanoparticles surface with the desired thiol derivative; on the other hand, the ligand exchange reaction allows to control the loading of the desired thiol derivative on the gold surface.^[74, 75]

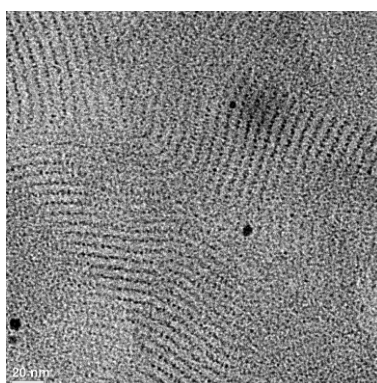


Figure 45 - TEM micrograph showing the 1.2-nm gold nanoparticles **A** appearing as organized in evenly spaced rows (that will be discussed in the next chapter).

The direct synthesis leads to nanoparticles **A** with an average diameter of $1.2 \pm 0.4 \text{ nm}^2$) (**Figure 45**). A few considerably larger particles (up to 7 nm) are visible in the TEM image (**Figure 45**). The ligands exchange reaction (synthesis of gold nanoparticles with 1-dodecanethiol followed by exchange of 1-dodecanethiol with compound **1**) leads to nanoparticles **B** with an average diameter of $1.7 \pm 0.4 \text{ nm}^3$) (**Figure 46**). The main advantages of the latter approach are: 1) the size of the gold nanoparticles can be controlled (first step), and 2) the ligands ratio can be adjusted (second step).

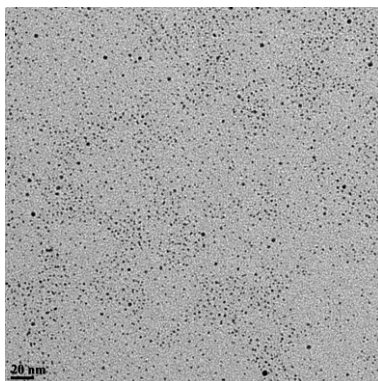


Figure 46 - TEM micrograph showing 1.7-nm gold nanoparticles **B**

The structure and purity of the gold nanoparticles were confirmed by ^1H -NMR spectroscopy (**Figure 47** and **Figure 48**): broadening of the peaks for the thiol derivatives grafted on the gold surface and disappearance of the CH_2SH signal^[72, 73, 76] are proof that the ligands are grafted onto the gold surface. For particles **B**, the relative amount of ligand **1** with respect to 1-dodecanethiol was estimated from the spectrum of the mixed system (part D of **Figure 48**), and was found to be *ca.* 40%. Finally, the absence of sharp peaks indicates the absence of free thiol in the samples.

²) Size and size distribution were estimated from a sample of 1755 particles (minimum size: 0.74 nm, maximum size: 6.98 nm).

³) Size and size distribution were estimated from a sample of 2575 particles (minimum size: 0.70 nm, maximum size: 5.31 nm).

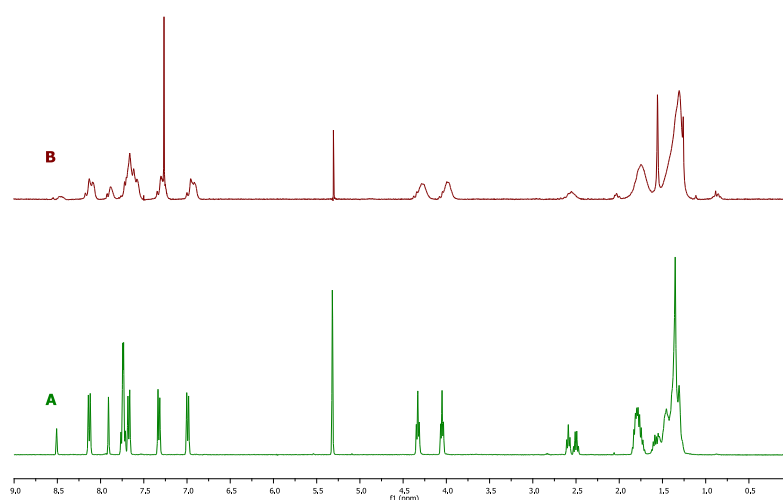


Figure 47 - ^1H -NMR spectra (in CD_2Cl_2) of compound **1** (part A), and gold nanoparticles **A** (part B)

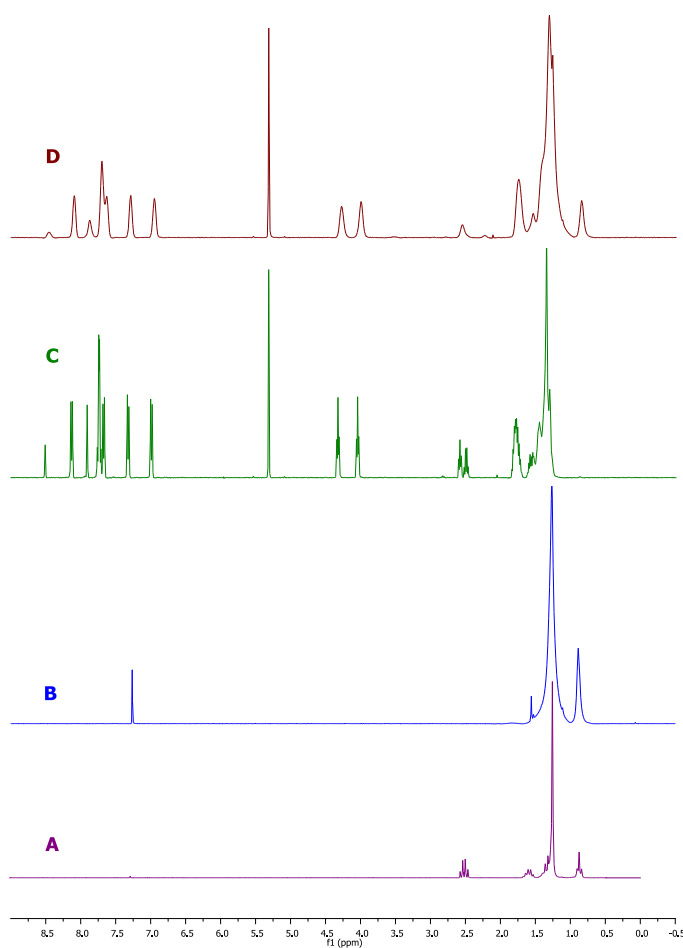
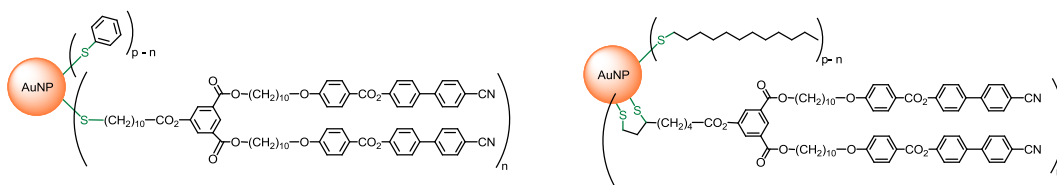


Figure 48 - ^1H -NMR spectra of 1-dodecanethiol (part A, in CDCl_3), dodecanethiol-stabilized gold nanoparticles (part B, in CDCl_3), compound **1** (part C, in CD_2Cl_2), and gold nanoparticles **B** (part D, in CD_2Cl_2)



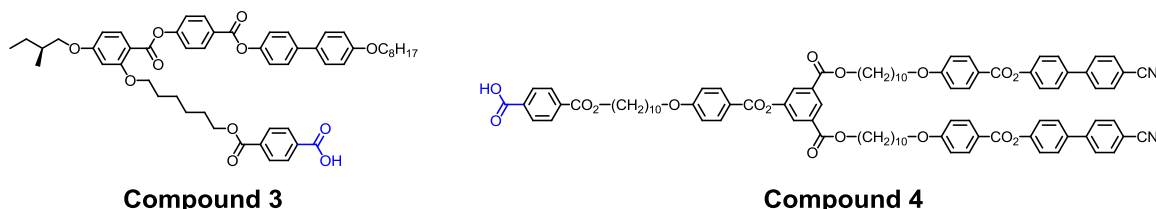
Scheme 11 – The synthesis of these particles (left: Au/BT±G₁CB–SH, and right: Au/C₁₂H₂₅–SH±G₁CB–S₂) failed by ligand exchange. The possible reasons are steric bulk on the one hand and destabilization of the gold core by the dithiol binding strategy on the other hand.

The ligand exchange with G₁CB–SH was tested on benzenethiol (BT)-stabilized AuNPs to yield Au/BT±G₁CB–SH (see **Scheme 11**, left). Unfortunately it did not lead to the expected product. A possible explanation could be the combination of the BT steric bulk that prevents the ‘easy’ access to the Au core for G₁CB–SH, and a too low incoming G₁CB–SH ratio in this bulky situation (the same ratio was however used in the preparation of particles **B**, **Scheme 10**). Similarly, different attempts were made to stabilize AuNPs with compound **2** (see Au/C₁₂H₂₅–SH±G₁CB–S₂ in **Scheme 11**, right) but even with the supposed stronger binding force of the two anchoring sites if compared to the thiol, they all failed as they lead to particles agglomeration. An explanation could be stated as Scott *et al.* showed that,^[77] in contrast to what could be expected, strategies to increase ligand-metal interactions by incorporating more thiolate linkers into the ligand must also take into account the packing efficiency and/or stability of such ligands on the metal surface, which can make them much more prone to oxidation under ambient conditions. This effect might have lead to particle miscoverage, a weaker stabilization (opposed to a better anchorage) and the final growth of particles making them less soluble finally leading to precipitation.

The compounds presented in this part were observed under POM and analyzed by DSC but none of them exhibited a mesophase neither particles including 100 % of LC ligands (particles **A**) nor those with fewer LC ligands (particles **B**). Therefore, in this case, it appears that this is not only the proportion of the attached LC ligands on the particle surface that is important for realization of a mesophase. It is possible that the core size (despite they are relatively low: 1.2 and 1.7 nm) combined with the rather elevated phase transition temperatures of the dendrimer used did not favor mesomorphic properties. Also, it is possible that the viscosity of the sample was too high, such that the formation of a mesophase was strongly kinetically hindered.

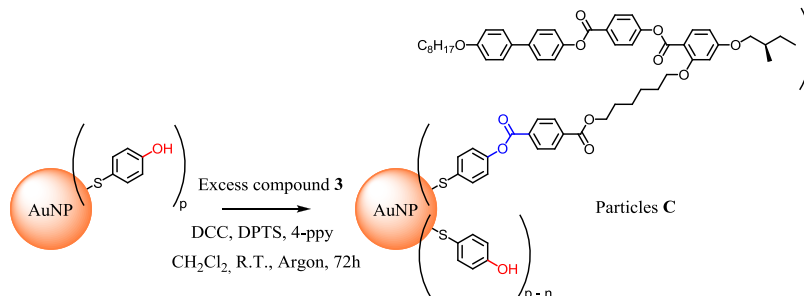
3.4.2. Esterification on AuNPs

Liquid-crystalline dendrimer-functionalized AuNPs were prepared through an esterification between AuNPs bearing hydroxyl groups in their ligand shell and mesogens or 1st-generation dendrimers bearing carboxylic acid groups as starting materials leading to functional hybrid materials (**Scheme 12**).

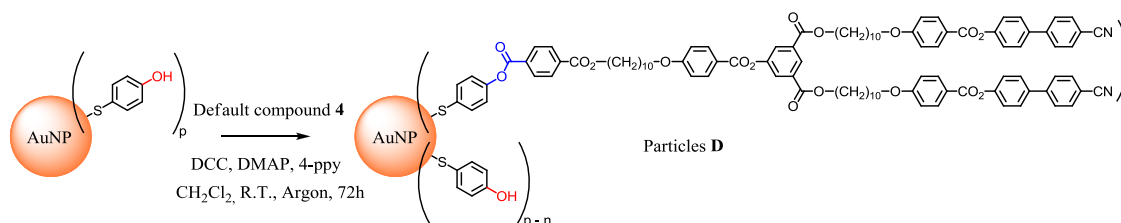


Scheme 12 – Mesogen (compound **3**) and first-generation dendron (compound **4**), both bear a carboxylic acid function allowing them to be esterified on hydroxyl-functionalized AuNPs.

The starting AuNPs are prepared according to the well-established Brust procedure^[78] with alcoholic end-functionalized thiolated aromatic ligands. In this manner dendrimers bearing a carboxylic acid group can be esterified on the available hydroxyl groups onto gold particles (**Scheme 13** and **Scheme 14**).



Scheme 13 – Compound **3** is esterified on pMP-stabilized AuNPs to yield particles **C** where all the available -OH groups are not esterified thus limiting the number of mesogens **3** on the AuNPs.



Scheme 14 – Compound **4** is esterified on pMP-stabilized AuNPs to yield particles **D** where all the available OH groups are not esterified thus limiting the number of dendrons **4** on the AuNPs.

AuNPs that are synthesized according to Brust *et al.* one-phase method^[78] leading to full coverage of the gold core with stabilizing alkane-thiol ligands – namely 4-mercaptophenol (pMP). The size of the particles could be modulated *via* the ratio of ligand to gold, the temperature as well as the nature and concentration of the reducing agent.^[73] On the AuNPs surface predominantly hydroxyl groups are exposed to the surrounding medium, which leads to rather different solubility compared to the free pMP ligand. This helps purification considering that pMP ligands are well soluble in dichloromethane whereas the particles formed are soluble in polar solvents (especially alcohols).

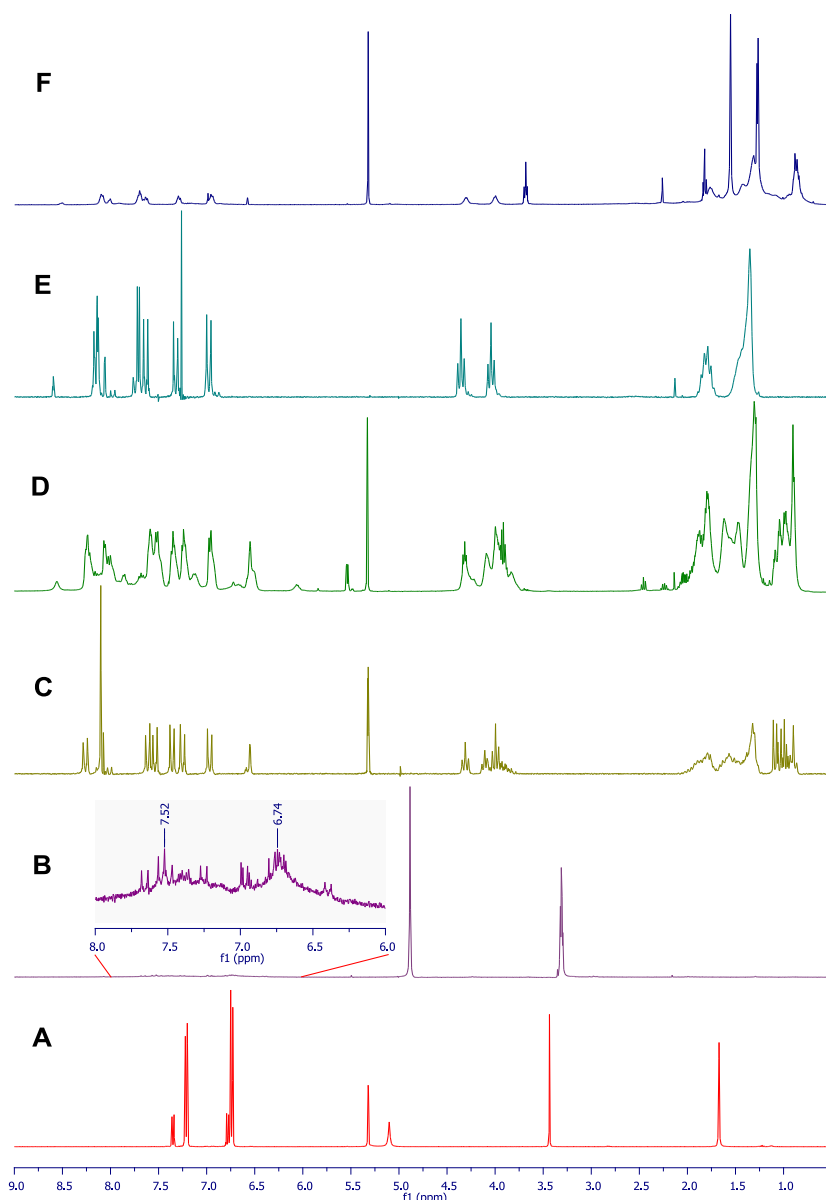


Figure 49 - ¹H-NMR spectra of 4-mercaptophenol (**A**, in CD₂Cl₂), 4-mercaptophenol-stabilized gold nanoparticles (**B**, in CD₃OD), compound **3** (**C**, in CD₂Cl₂), gold nanoparticles **C** (**D**, in CD₂Cl₂), compound **4** (**E**, in CDCl₃), gold nanoparticles **D** (**F**, in CD₂Cl₂)

Particles **C** (particles **D**): pMP-stabilized AuNPs are combined together with compound **3** (compound **4**) to form a new system made of esterified and non-esterified mercaptophenol groups as probed by NMR spectrum in **Figure 49-D** (in **Figure 49-F**). Indeed a broad hump observed in the AuNP spectra under the aromatic peaks suggests that there remain not esterified pMP but yet it was not possible to estimate their proportion as the global integration of the aromatic part of the spectrum corresponds to that of compound **3** (compound **4**).

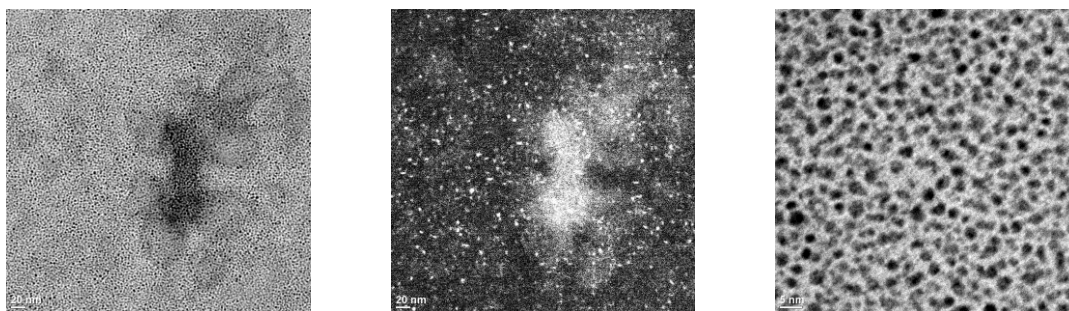
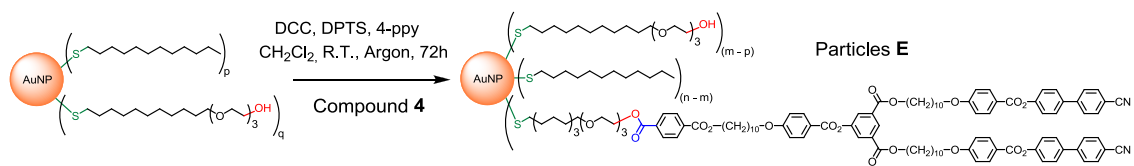


Figure 50 – TEM micrographs of esterified AuNPs (Au/pMP}G1CB-COOH)

Particles under consideration are about 1.9 nm, this corresponds to about 205 gold atoms for the core of which about 112 lie on the surface and considering 20 % of organic layer, there are about 80 pMP ligand per particle. Then the molecular weight is *ca.* 50.5 kg.mol⁻¹ and G₁CB-COOH dendron is *ca.* 1.5 kg.mol⁻¹. As a consequence 80 equivalents were used with respect to the gold particle amount; this was set as the ‘100 %’ reaction. 10 reactions were lead decreasing the loading by 10 % steps: the subsequent esterification reactions were done with a default of ligand so that all the available OH functions were not reacted. Particularly the ‘40 %’ reaction was achieved and corresponds experimentally to an equivalent mass of particles and dendrons involved in the esterification reaction. Nevertheless this decreasing in the dendron loading led to the loss of the particle organization at the nanoscale (see next chapter on assembly).



Scheme 15 - Reaction scheme of the esterification of compound **4** (G₁CB-COOH) bearing a carboxylic acid function on AuNPs bearing a limited number of hydroxyl functions (Au/C₁₂H₂₅-SH±mud3eg). The resulting AuNPs (Particles **E**, Au/C₁₂H₂₅-SH±mud3eg}G₁CB-COOH) have about 9% of LC moieties in their shell.

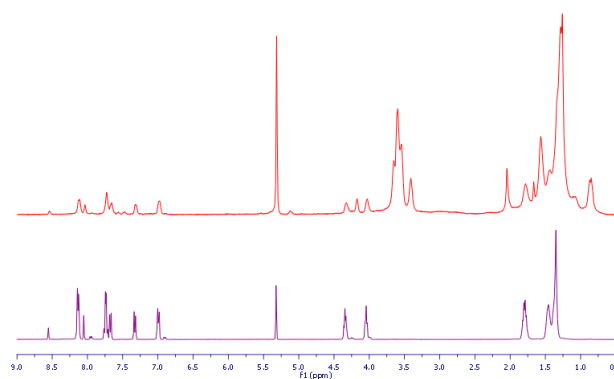
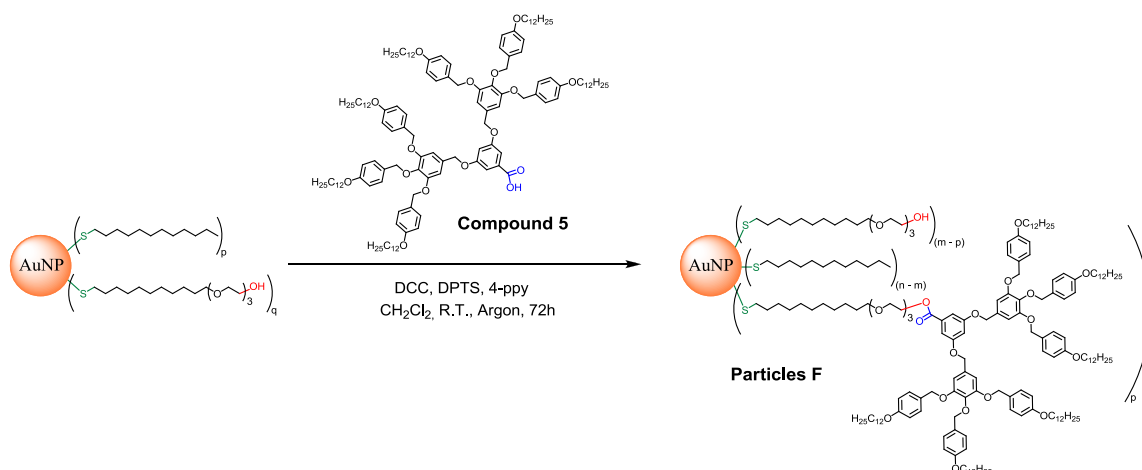


Figure 51 – ^1H -NMR spectra of compound **4** (bottom, in CD_2Cl_2) and compound **4** esterified on $\text{Au/C}_{12}\text{H}_{25}\text{-SH}\pm\text{mud3eg}$ leading to particles **E** ($\text{Au/C}_{12}\text{H}_{25}\text{-SH}\pm\text{mud3eg}\}\text{G}_1\text{CB-COOH}$).

It was possible in the case of particles **E** ($\text{Au/C}_{12}\text{H}_{25}\text{-SH}\pm\text{mud3eg}\}\text{G}_1\text{CB-COOH}$) to estimate the number of esterified compound **4**. The proportions of the different ligands (in initial particle size of 1.54 nm) are 44 % $\text{C}_{12}\text{H}_{25}\text{-SH}$ (20 ligands), 47 % mud3eg (25 ligands), and 9 % compound **4** (4 ligands)



Scheme 16 – Pathway of the esterification of G_2 polybenzylether dendrons bearing a carboxylic acid function (**Compound 5**) on AuNPs bearing a limited number of hydroxyl functions. The resulting AuNPs (**Particles F**) have about 17% of LC moieties in their shell.

Particles **F**: mixed monolayer of (11-mercaptoundecyl)triethylene glycol- (mud3eg-) and dodecanethiol-stabilized AuNPs are combined together with compound **5** to form a new system made of esterified and non-esterified mud3eg groups as probed by NMR spectrum in **Figure 52**.

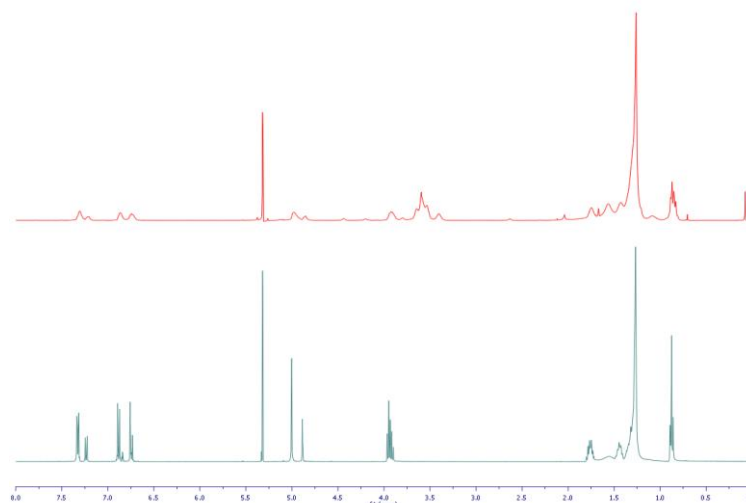
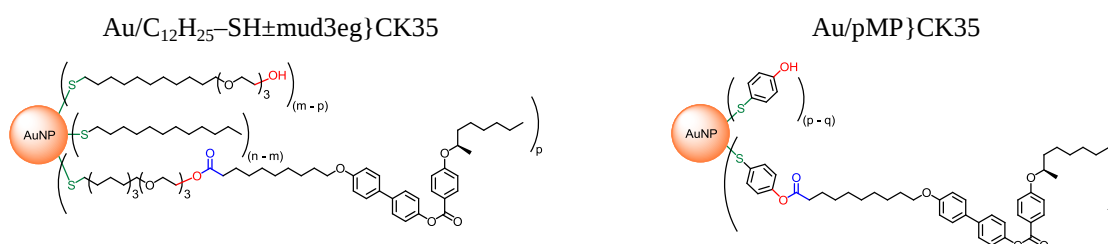


Figure 52 - ^1H -NMR spectra of compound **5** (bottom, in CD_2Cl_2), and AuNPs **F**. (top, in CD_2Cl_2) after purification by ultrafiltration.

As a result, the top spectrum in **Figure 52** was integrated with respect to the signals of compound **5** and a ratio of about 1:4 was found from the 3.41 ppm signal (mud3eg). It corresponds to about 17 % compound **5** (15 ligands), 53 % mud3eg (46 ligands), and 30 % $\text{C}_{12}\text{H}_{25}\text{-SH}$ (26 ligands).

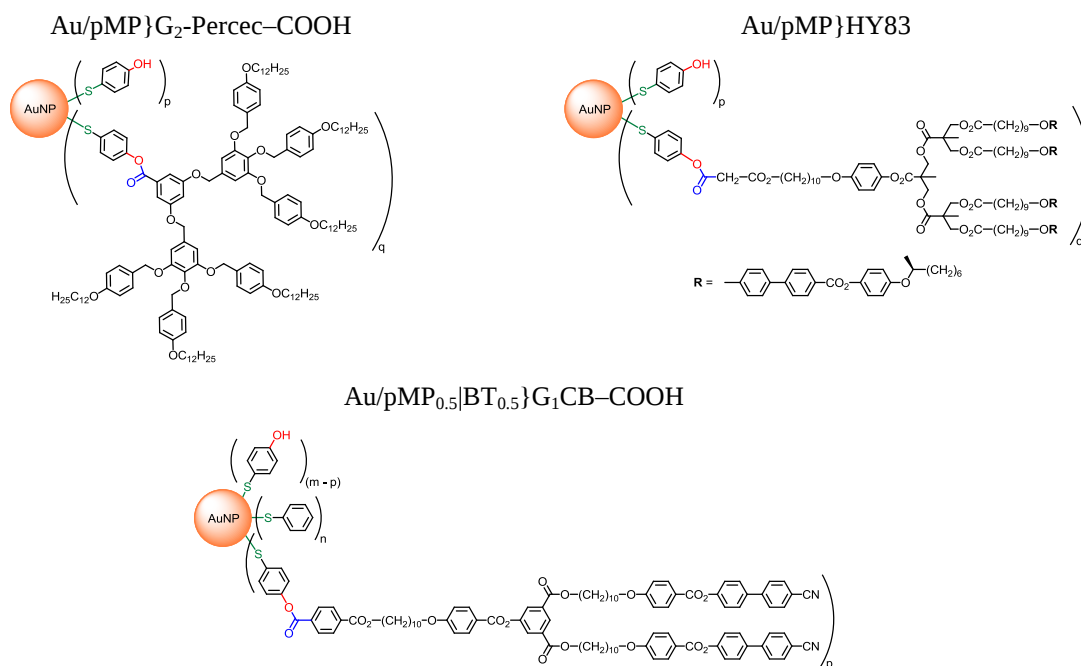
In addition, many other combinations of AuNPs bearing other mesogens have been tested but they did not lead to the coupling. They either aggregated (consequently led to insoluble compounds) or had a too low yield. Some examples are shown in **Scheme 17**.



Scheme 17 – Illustration of some targeted composites including chiral G_0 mesogens whose synthesis did not work.

The chiral mesogens CK35 was successfully grafted neither on the ethylene glycol groups nor on the aromatic pMPs. On the other hand particles $\text{Au/C}_{12}\text{H}_{25}\text{-SH}\pm\text{mud3eg}$ and Au/pMP have been good precursors to carry out the esterification reaction with other liquid-crystalline ligands. For the CK35 mesogen, the aliphatic acid is certainly less favorable than benzoic acid (compound **3**) because the hydroxyl group of the carboxylic

acid is a poor leaving group. It might be replaced by another nucleophilic group to form an acyl chloride for example.



Scheme 18 – Illustration of the one 1st and two 2nd generation dendrimer-based AuNPs that were inaccessible with the esterification reaction.

It is supposed that Au/pMP}HY83 (see **Scheme 18** top right) was not formed for similar reasons than the CK35 did not bind (**Scheme 17**), an acyl chloride or a terminal benzoic acid would have probably lead to that material. Concerning Au/pMP}G₂-Percec-COOH (**Scheme 18** top left), the fact that the carboxylic acid was directly bound to the G₂ dendrimer core plus its steric bulk was certainly unfavorable for the chemical reaction. It could be compared to the results for particles **F** where the stabilizing ligands on AuNPs act as spacers from the Au core and thus facilitate the esterification. Finally Au/pMP_{0.5}|BT_{0.5}}G₁CB-COOH (**Scheme 18** bottom) could not be prepared probably because of a too low ratio of pMP to BT. Indeed it was not possible to estimate the ratio on the particles because both ligands are too similar and proton resonances were too broadened as they are very close to the Au core.

Generally speaking, the more functional groups on the particle surface the greater the chances of esterifying dendrimers. Yet in the case of particles **A** (**Scheme 9**), a full coverage with dendrimers has not proven to be helpful in obtaining mesomorphic properties whereas in a lower coverage of dendrimers such behavior was observed (**Figure 53**).

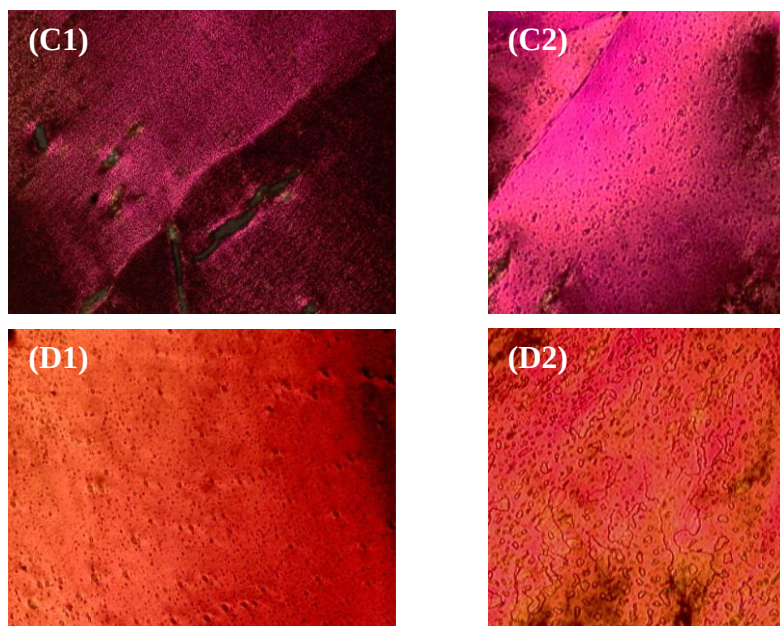


Figure 53 – POM micrographs of the textures displayed by particles **C** (Au/pMP) $\{G_1CB-COOH\}$, (C1) 75 °C 100x magnification, (C2) manual zoom in on a lighter region of the sample at 113 °C; and particles **D** (Au/pMP) $\{G_1CB-COOH\}$ (D1) 140 °C 100x magnification, (D2) manual zoom in on another region of the sample at 149 °C.

The composites resulting from the esterification reaction (particles **C** and **D**) were observed under POM and displayed a distinct mesophase but of unknown nature (see **Figure 53**). They could possibly be some nematic phase because dark crosses can be distinguished (see D2 in **Figure 53**) and remind of the nematic phase schlieren texture. Unfortunately these observations were not confirmed by DSC analysis as no phase transition temperature was determined. In this case the particle Au/pMP diameters were greater than those observed in the case of direct synthesis or ligand exchange and yet lead to the observation of a mesophase. Therefore the size does not seem to be the most influential parameter (to some extent). The dendrimer for particle **D** is of the same nature as those used in particles **A** and **B** so it could be hypothesized that the ligands stabilizing the particles have a non-negligible influence on the mesomorphic properties of these hybrid compounds. For particles **C**, the smaller weight and architecture (laterally branched) may have favored the formation of a mesophase obtained from the same precursor particles (Au/pMP).

3.4.3. Purification methods

3.4.3.1. Size-exclusion chromatography

Bio-Rad Bio-Beads SX-1 and Sephadex LH-20 were used as a size exclusion chromatography media to gather purified dendrimer-derivatized AuNPs. More details concerning both resins are given in the First appendix.

Different techniques were used to purify the nanoparticles depending on the preparation method. For the direct synthesis, the nanoparticles were purified by size exclusion chromatography. For the exchange reaction, the nanoparticles covered with 1-dodecanethiol were purified by membrane filtration and the final materials by ultrafiltration. In addition, the particles core size was estimated to be lower than *ca.* 2 nm by UV-Vis spectroscopy (no plasmon band located at *ca.* 520 nm) and further validated by TEM observations (**Figure 45** and **Figure 46**).

3.4.3.2. Ultrafiltration

Whether it is by centrifugation or N₂ pressure, ultrafiltration (UF) seems to be a technique only little applied as judged from the literature. However after discussions in conferences with other people working in the field of NPs, it seems that many people tried this technique without success. According to our own experience, this technique turned out to be the most effective to cleanse the final products instead of exclusion chromatography.

Final materials made of dendrimer-functionalized AuNPs (Particles **A**, **B**, **C**, **D** and **E**) were subjected to ultrafiltration. Indeed this technique allows one to separate particles from unreacted dendritic ligands in a mild fashion. More information about UF is given in the First appendix.

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4. Assembly of LC-dendrimer-containing AuNPs

4.1. Self-assembly at stake

Forces inducing self-assembly are better understood as soon as the phenomena giving birth to them are explained. Indeed if self-organization appears without an outer influence, forces are required to induce this self-organization and it occurs only when these forces are already present in the system. For nanometer scale objects, weak forces (capillarity, wetting, van der Waals forces) predominate in self-organization process. Moreover, self-organizations are obtained from a nanoparticle solution deposit on a flat substrate leaving the solvent evaporate. First, particle-particles, particles-solvent, particles-substrate interactions are considered in 2D and 3D network formation. Otherwise, the solvent in which the nanoparticles are dissolved has an influence on the wetting issue. Indeed, when a drop is casted it is obvious that the wetting of the liquid on the surface as well as its evaporation are going to have a major influence on the final structure. At a lower scale, the liquid interacts with the substrate and nanoparticles through the capillarity forces. Finally far weaker electrostatic forces, the so-called van der Waals forces, lead to interaction when charged species are involved or when steric repulsions due to the particle coating are concerned. The coating molecules form not only a protective layer but also prevent direct contact between particles and thus particle coalescence, they also participate to the reinforcement of the network.

The following description of the self-assembly phenomenon mainly follows the description of Pileni *et al.* as they intensively studied this field of research for silver, gold, and other metal sulfide nanoparticles.^[1-4]

4.1.1. Wetting and capillary forces

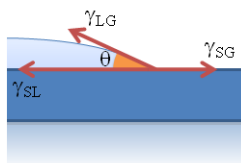


Figure 54 – The contact angle θ is measured between the liquid-gas and solid-liquid interfaces (γ_{ij} being the surface energies between the indicated interfaces): the more the contact angle is high, the less the spreading is good. The spreading parameter $S = \gamma_{SG} - (\gamma_{SL} + \gamma_{LG})$ combined with Young's relation gives $S = \gamma_{LG} (\cos \theta - 1)$ having physical solutions only in case of partial wetting ($S < 0$).

Both wetting and capillary forces are determined by the surface tension. The whole system tends to minimize interfacial energy γ consequently lowering the contact angle θ (**Figure 54**). The wetting state of the medium on which particles are deposited plays an important role on particle organization.

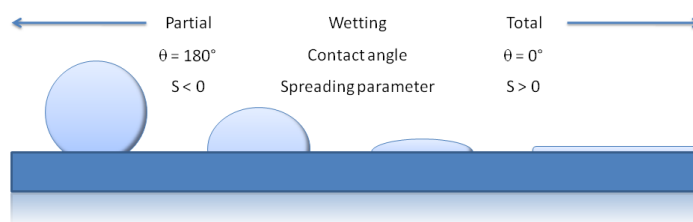


Figure 55 – Illustration of the different cases of wetting and the associated notions of contact angle and spreading parameter.

In the case of total wetting (spreading parameter $S > 0$, right side of **Figure 55**), particles are dispersed correctly on the surface over a large area. The deposit is homogeneous in this case but deficiencies may appear if particle concentration is too low. At the opposite, partial wetting ($S < 0$, left side of **Figure 55**) creates a drop over the surface. While evaporating, this latter tends to decrease its size and progressively concentrating particles at the centre of the drop. The resulting deposit is inhomogeneous and particles form a big aggregate rather than a homogeneous film.

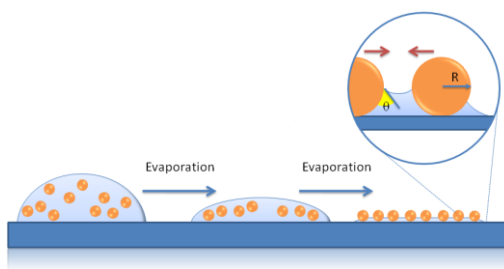


Figure 56 – Illustration of capillary forces resulting from the bridge formed when the solvent evaporates and tends to gather together particles. **R** is the particles radius and **θ** the angle between the liquid and particle surface at the contact point.

Let us consider particles deposited on a substrate but still surrounded by solvent. Because of evaporation and as soon as the quantity of solvent becomes very thin, a liquid meniscus is created forming a bridge between particles (**Figure 56**). Because of the liquid surface tension, that meniscus exerts a capillary force given by **Equation 2**.

$$F = 4\pi R \gamma \cos\theta$$

Equation 2 – **F** is the capillary force, depending on the radius of particle **R**, the surface tension γ and the angle θ between the liquid and particle surface at the contact point. As examples, $\gamma = 9.6 \cdot 10^{-5} \text{ J.m}^{-2}.\text{K}^{-1}$ for hexane and $\gamma = 1.5 \cdot 10^{-4} \text{ J.m}^{-2}.\text{K}^{-1}$ for water.

That force tends to gather particles and favors a compact assembly and if it becomes predominant it favors 3D particle network locally concentrating particles instead of creating a film (2D) organization. Through both phenomena, any case can be imagined: from particles spread all over the surface to localized aggregates. Hence the importance of a good estimation of the scale of sizes of these phenomena is necessary to predict and to explain experimental results.

4.1.2. Dispersion forces and van der Waals interactions

At the nanometer scale particles, solvent and substrate interact *via* dispersion forces. These forces are due to attractive interactions at short distances between molecules and they are described by fluctuations of their electronic densities. Indeed under thermal agitation, the variation of the electronic density induces a moment. This moment interacts with the electronic cloud of a neighbor molecule subsequently inducing a dipole whose fluctuations are synchronized with those of the first molecule. The induced dipoles have the same direction and a permanent short distance attraction is established. These are the so-called London interactions, arising besides the van der Waals interactions. It originates

molecule cohesion and depends on the molecule polarizability, thus depending on the molecule number of electrons. Macroscopic interaction is the result of the sum of any interaction between pairs of molecules available in the system. This calculation takes intrinsically into account the system geometry and potential between molecules. The factor grouping polarizability terms and electronic densities of molecules is the so-called Hamaker constant A .^[5, 6] This constant is used to calculate the interaction energy between particles of a given material in **Equation 3**.

$$E_{vdW} = \frac{A}{12} \left(\frac{4R^2}{C^2 - 4R^2} + \frac{4R^2}{C^2} + 2 \ln \frac{C^2 - 4R^2}{C^2} \right)$$

Equation 3 – Interaction energy between particles is given by van der Waals energy E_{vdW} . A is the Hamaker constant, C is the particle center-to-center distance and R the particle radius. For example A has a value close to $3.04 \cdot 10^{-19}$ J for two silver particles and $4.00 \cdot 10^{-19}$ J for two gold particles.

The Hamaker constant is also used to explain the influence of the substrate on the self-organization of the nanoparticles. A medium presenting attractive interactions with deposited particles favors the formation of extended monolayers but less compact whereas a medium presenting repulsive interactions favors monolayers as well but also the formation of aggregates. In the case of silver nanoparticles deposited on a carbon grid, the interactions are attractive.^[7-9] As an example particles covered by alkyls can be considered. As soon as the length of the alkyl coating surrounding the particles decrease, less extended monolayers are favored with a fixed distance between particles. This distance corresponds to the length of a dodecanethiol chain, namely 1.8 nm. This means that chains are interpenetrating in the case of dodecanethiol covered nanoparticles, whereas for shorter alkanethiols-coated nanoparticles (decanethiol or octanethiol), chains do not interpenetrate any more. It could be considered that the shorter the chains are, the stronger the interaction with the substrate becomes. The latter being attractive, particles cannot easily move any more on the substrate and it explains a bigger distance between particles, that is to say a distance longer than the length of a chain.

The steric repulsions of organic molecules (thiolated alkane chains) passivating particles play an important role into 2D and 3D network construction. Steric repulsion potential is given by **Equation 4**.

$$E_{steric} \approx \frac{100R\delta_{SAM}^2}{(C-2R)\pi\sigma_{thiol}} kt \exp\left(\frac{-\pi(C-2R)}{\delta_{SAM}}\right)$$

Equation 4 – R particle radius, C distance between particles center to center, δ_{SAM} thickness of the alkane film (18 Å for dodecanethiol), σ_{thiol} surface occupied by thiols (4.3 Å² for dodecanethiol).

Interparticle interaction potential results from the sum of van der Waals interactions (E_{vdV} , **Equation 3**) and steric repulsion potential between alkane chains (E_{steric} , **Equation 4**). Particles organize as soft spheres with an effective diameter including the organic coating. Particles self-organize provided that steric stabilization of organic molecules is enough compensated by van der Waals interaction.

4.1.3. Bénard-Marangoni-type instabilities

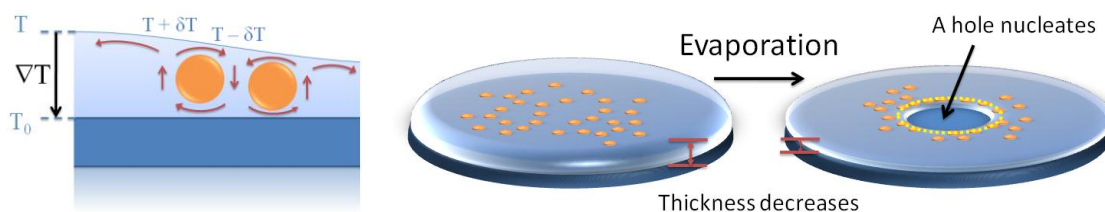


Figure 57 – Left: Schematic illustration of the Marangoni effect due to evaporation (adapted from Maillard *et al.*^[10]). A temperature gradient is created across a film of volatile solvent and it results in a convective flow through the film around the particles in a hexagonal pattern of convection leading to hexagonal arrangements of nanoparticles. Right: Long-range convections in the liquid film can lead to the rupture of the latter and a hole nucleation process appears where particles are pushed out along the hole advancing rim (adapted from Ohara *et al.*^[11]).

The solvent evaporation process is important and is related to the solvent evaporation velocity. Indeed, a study showed the influence of the evaporation speed of solvents on the organization of nanoparticles.^[3, 10] It was showed that a drop deposit of ferrite particles dispersed in hexane on a microscopy grid hold on by anticapillary twizers gives rise to micrometric rings, the surrounding of which is composed by nanoparticles. If these particles are dispersed in decane, what decreases considerably evaporation velocity, a random dispersion of particles is observed without the appearance of rings. This phenomenon was attributed to Marangoni instabilities:^[10, 11] these latter are related to a gradient of surface tension in a liquid medium generating periodic convection fluxes. A strong evaporation rate (as in the case of hexane) favors these instabilities and the formation of rings (a representative example is given in **Figure 58**). Then, single holes

have abnormal high local nanoparticle densities. This is explained by the convective flow and the capillary forces which drags nanoparticles and further increases the local high-density areas by the hole nucleation process during the film retraction. This phenomenon was already observed for a wide variety of materials such as silver, silver sulfide or cobalt.^[10, 12]

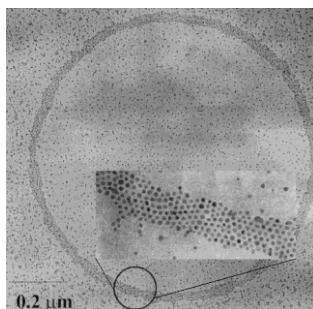


Figure 58 – TEM micrograph of rings of 2.5-nm silver nanoparticles obtained from evaporation of a hexane solution. The inset shows a magnification of the particle organization in the area of the ring. Taken from Ref. ^[11]

4.1.4. 2D and 3D nanomaterials arrangements

Spontaneous assembly of uniform-size spheres in a regular network is a universal phenomenon observed for objects from relatively small diameter to a relatively wide scale: from atom (10^{-8} cm), to molecules and macromolecules (10^{-6} cm, proteins, polymers, colloids, etc.) to opals and synthetic spheres (10^{-5} cm) and even to any spherical object (1 up to 10^2 cm) like balls, fruits. The parameters from the radiocrystallographic structure of a given substance include not only its intrinsic structure (shape, size), its hardness, that is to say its compressibility and deformability, but also the nature and the range of interactions between substances. In the extreme case of “hard spheres” where the contact between spheres is possible, compact crystallographic structures such as centered face cubic (cfc) or hexagonal compact (hcp) are possible. They have the highest possible compacity rate (74%) and the highest coordination number (12). Metallic nanomaterials and semiconductors coated by organic molecules (alkane chains) are considered as “soft spheres.”

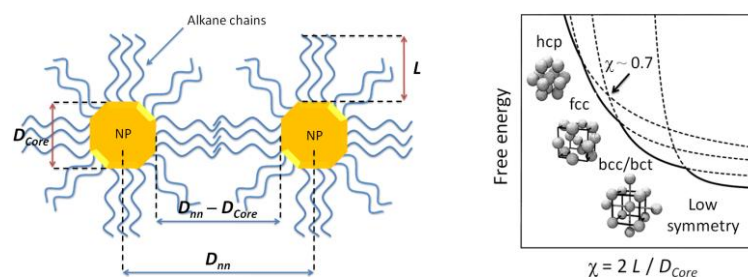


Figure 59 – The parameter for the structure of an assembly of nanometer-scaled particles covered by carbon chains is defined by $\chi = 2L / D_{Core}$ as defined in the left figure. According to this parameter different structures were observed experimentally, the highest values of χ are related to the highest symmetries (right). Taken and adapted from Whetten.^[13]

These soft spheres are characterized by a short-range attractive potential, low symmetrical crystallographic structures, and thus a lower coordination number is preferred. χ is a parameter defined by $\chi = 2L / D_{Core}$ where D_{Core} is the diameter of the nanomaterial core and L the thickness of the coating of alkane chains (**Figure 59**). According to the values of χ different crystallographic structures were observed for different nanomaterial networks such as silver, gold or palladium.^[13, 14] Nevertheless these results do not take into account the conformation of the alkane chains and the possible presence of defects on it. Thus, it was observed that in the particular case of silver sulfide particles^[8] that on the one hand alkanethiol chains ($C_nH_{2n+1}-SH$) for $n < 8$ do not grab on the surface of particles due to a high number of defects on the chain and on the other hand for longer chain lengths ($n = 14$) the presence of defects at the end of the chains keep 2D organization but prevent 3D assembly (**Figure 60**, left).^[15] When nanomaterials coated with alkane chains self-organize in 2D hexagonal network, the interparticle distance corresponds to the alkane chain length. It suggests an interdigitation of the chains. The best case is reached when the alkane chain are able to compact, what strengthens the network. Finally, an important parameter to the crystalline structure of 2D and 3D arrangements is the nanomaterial facet morphology. Indeed, the alkane chain distribution on the surface of particles when they have facets is not uniform. An arrangement is favored in the case of a configuration where particle crystalline faces are parallel to each other.^[16] It allows a maximum compacity effect of the chains (**Figure 60**, right).

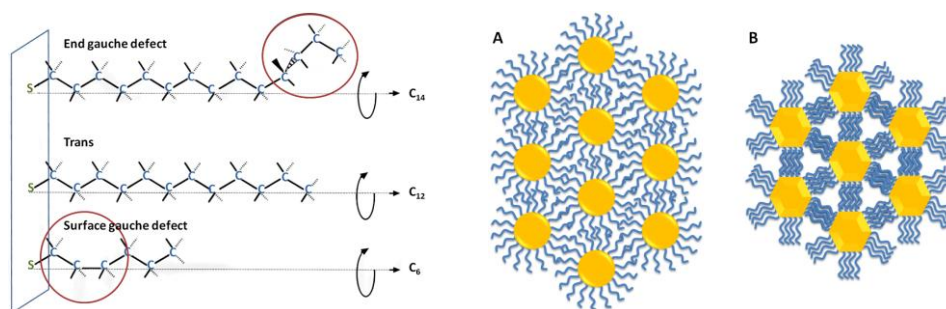


Figure 60 – Left: Schematic representation of the conformation and defect of thiol derivatives with different alkyl chain length. Taken from Ref. ^[15]. Right: Schematic representation of self-organized superlattices of spherical (A) and faceted (B) particles: The macroscopic properties of the NPs are determined not only by the properties of each individual particle but by the coupling/interaction between nanoparticles interconnected and isolated by a monolayer of thin organic molecules. Adapted from Wang.^[16]

The transmission electronic microscopy (TEM) allows one to characterize the nanoparticles and their arrangements provided that the film obtained is thin enough (i.e. the stacking of a few monolayers of particles). In the case of multilayer arrangements, X-ray diffraction appears as the best technique. Wide-angle X-ray spectroscopy (WAXS) is directly related to the atomic structure of the nanomaterials, whereas small-angle X-ray spectroscopy (SAXS) gives access to the nanomaterial order in the 3D network. As an example, 3D networks were obtained with 7.2-nm cobalt nanoparticles, with a low size distribution (10%) corresponding to more than 300 layers of particles.^[17] A hexagonal network is obtained in this case.

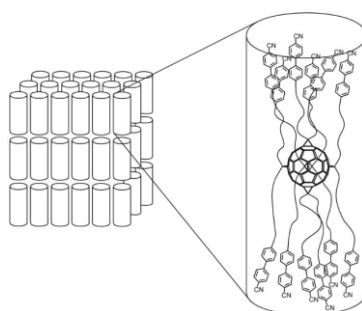


Figure 61 – Proposed supramolecular organization of cyanobiphenyl derivative-capped fullerenes. The formation of a smectic A phase indicates that the cyanobiphenyl units are not oriented radially around C₆₀ but form a cylinder-like structure with the mesogenic fragments oriented upward and downward. Such a structure favors the formation of layers. Taken from Chuard and Deschenaux.^[18]

A non-metallic analogue to metallic particles is the fullerene whose supramolecular organization for liquid-crystalline derivatives can be explained as follows: the C₆₀ unit is

embedded in the dendritic core which is oriented parallel to the layer planes, and the mesogenic units orient above and below the dendritic core. Interdigitation occurs from one layer to the adjacent one (**Figure 61**). Derivatives bearing cyanobiphenyl units gave rise also to supramolecular organization: the formation of a smectic A phase indicates that the cyanobiphenyl units form a cylinder-like structure with the mesogenic fragments oriented upward and downward. Such structures favor the formation of layers. The mesomorphic properties of such compounds indicate that when the anisotropy is restored around the C₆₀ unit, liquid crystalline behavior takes place. This result is important taking into account the structural analogy between C₆₀ and gold nanoparticles. Indeed, both of them can be considered as sphere-like, isotropic structures.

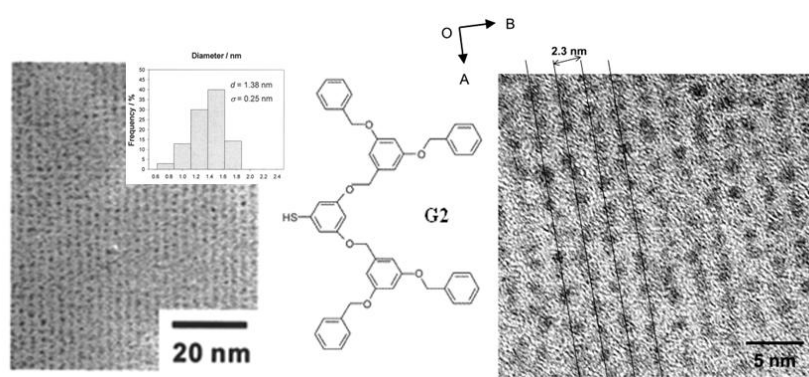


Figure 62 – TEM image and size distribution of Au/poly(oxymethylphenylene) dendron (PPD) composites (left); 2nd generation of PPD is presented (middle); HRTEM image showing AuNPs regularly aligned in the OB direction but not in the OA one (right). Taken from Nakao *et al.*^[19]

Torigoe and co-workers have prepared poly(oxymethylphenylene) dendrons of 1st to 4th generation with a thiol group to synthesize small AuNPs with narrow size dispersion.^[19] Interestingly G₁ and G₂ led to reproducible spontaneous formation of one-dimensional arrays on carbon films (a representative example for G₂ is shown in **Figure 62**).

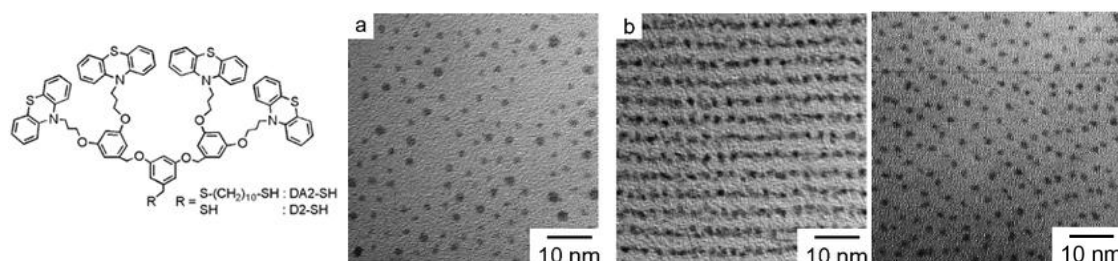


Figure 63 – Fréchet-type G₂ dendron with either a thiol or an alkylthiol chain terminated by a thiol function used for AuNPs synthesis (left); on the right, first TEM picture corresponds to the D2-SH system (lone SH)

function) while the last two images illustrates the particles arrangement of DA2-SH one (C_{10} alkyl chain). Taken from Komine *et al.*^[20]

Fujihara and co-workers observed AuNPs one-dimensional arrangements on carbon films provided that an alkyl chain spacer is present between the anchoring thiol function and the 2nd generation Fréchet-type dendrons (DA2-SH in **Figure 63**).^[20] In addition particles are very small plus have a very narrow size distribution (1.5 ± 0.1 nm).

Yamada *et al.* have synthesized gold nanoparticles functionalized by hexaalkoxy-substituted triphenylene (TP) as a discotic liquid crystalline molecule (Au-TP).^[21] The self-assembled structure of Au-TP could be controlled (1D or hexagonal closed packed (hcp) structures) by the ratio of the solvent used (methanol-toluene), triggered by the extent of the π - π interactions among the adjacent TP ligands on a particle surface. They have presented the distinct phenomenon that the gathering status of the surrounding organic ligands themselves in solution influences the self-assembled structure of metal nanocores on a substrate.

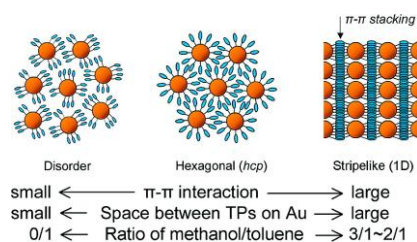


Figure 64 – The possible arrangement of Au-TP depends on factors investigated; π - π interaction, space around TPs on Au, and solvent hydrophilicity (ratio of methanol/toluene). Taken from Shen *et al.*^[22]

In another report, Yamada *et al.* emphasized the π - π interaction of the triphenylene (TP) moiety they used to synthesize a series of discotic liquid particle molecules.^[22] The stripe-like (linear 1D in row) self-assembly of Au/TPs can be achieved in a $0.5 \mu\text{m}$ area due to the formation of a column structure of TP originated from strong π - π stacking (**Figure 64**). Patterns of arrangements could be changed by tuning the degree of π - π interaction among TPs on adjacent Au-TPs to be stripe-like, hcp, or disorder. Changing the hydrophilicity of the solvent lead to a stripe-like arrangement of AuTP (see **Figure 64**), the following points were found essential: (1) the sufficient free space around the TP moieties, which easily allows the TP ligands on the adjacent AuNPs to intercalate. (2) The adjustment of the solvent hydrophilicity (ratio between methanol and toluene) to promote strong intermolecular stacking interaction of TP moieties among Au-TPs.

4.1.5. Mediated assembly of AuNPs

Recently, a new spotlight has been focused on block copolymers (BCPs), thoroughly studied for nearly half a century, because of their potential use in numerous nanotechnologies. This renewed interest is a consequence of the self-assembled microdomains characteristic of these materials. A recent review by Darling presents the alignment approaches for a given polymer morphology.^[23]

Block copolymers result from the chemical integration of two or more monomer units in random, alternating, or graft architecture chains. A block copolymer is comprised of alternating segments of polymer chains synthesized using living polymerization (ATRP, RAFT, ROMP). In a living polymerization, a polymer chain is first grown while maintaining an active end, after which a second monomer is added to grow a second block onto the pre-existing chain. If care is taken during the synthesis, the process can be carried out several times to generate highly monodispersed, complex polymer architecture.^[24] As an example, PS-*b*-PMMA is the short name for polystyrene-*block*-poly(methyl methacrylate) and it is made by first polymerizing styrene, and then subsequently polymerizing MMA from the reactive end of the polystyrene chains; this polymer is a “diblock copolymer” because it contains two different chemical blocks and triblocks, tetrablocks, multiblocks can be prepared.

If two polymers are blended, they will almost inevitably undergo a phase separation on the macroscale due to the unfavorable entropy of mixing two long-chain macromolecules. When a polymer chain is comprised of chemically connected, mutually immiscible or incompatible segments or blocks, the polymer can undergo what is termed microphase separation. Due to the physical connectivity of the two blocks, they cannot form large phase-separated domains, so instead the individual segments self-organize into domains with nanoscale dimensions. At certain chain lengths and volume fractions, the self-organized structures can have well-defined 2D or 3D periodicity consisting for example of ordered spheres, cylinders, lamellae and bicontinuous structures.

The length scale of separated domains and the architecture they adopt depends on the molecular weight, composition, interactions, and architecture of the segments and on the nature of any co-assembled additives, which may swell or cross-link the system.^[23]

The self-assembly of block copolymers films displays a marked sensitivity on the surface properties of a substrate. This occurs because the two polymer blocks have different

wetting characteristics, and it follows from this fact that the patterns generated by this route will have a periodic modulation in their wetting properties. This contrast in surface properties can be used quite impressively to selectively decorate block co-polymers domains with various types of vapor deposited metals as reported by Lopes and Jaeger.^[25] This procedure begins with a PS-*b*-PMMA block copolymer with blocks ratios such that it self-assembles as cylinders of PMMA in a PS matrix. It is cast as a very thin film on a Si₃N₄ substrate, such that the block architecture consists of a very thin PMMA layer wetting the substrate, a layer of PS matrix, and a monolayer of PMMA cylinders laying parallel to the substrate and exposed to the air interface. Therefore, the surface of the film displays alternating stripes of PMMA (cylinders) and PS (matrix).

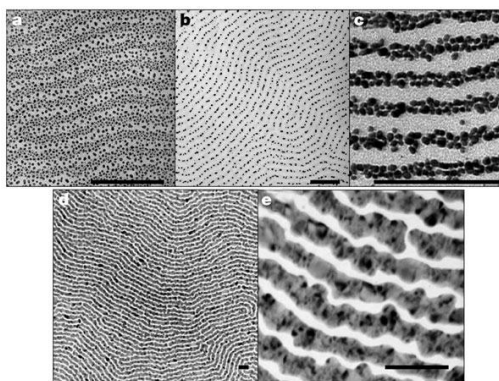


Figure 65 – Nanoscale decoration of phase-separated PS-*b*-PMMA block copolymer film on a silicon nitride substrate by selective wetting and accretion of a vapor deposited metals like gold (**a-c**) and silver (**d** and **e**) selectively in the PS phase. **a** is as deposited, **b** is annealed, **c** is repeated deposition and annealing, **d** is a large area and **e** a close-up view. Scale bars are 200 nm in **a-c** and 100 nm in **d** and **e**. Taken from Lopes and Jaeger.^[25]

When a small amount of metal is thermally evaporated onto this self-assembled pattern, the different wetting characteristics of the two polymer blocks will cause the metal atoms to preferentially accrete in one of the domains. By annealing the sample above the glass transition of the polymer, the deposited metal can be driven exclusively in one block (**Figure 65, b** and **c**). In the case of gold we see that even without annealing, the metal atoms have a distinct affinity for the PS phase (**Figure 65a**). After annealing, it is evident that the gold has migrated exclusively to the PS domains (dark stripes in **Figure 65b** and **c**). Further deposition and annealing increases the gold loading on the PS stripes, eventually forming nanowires composed of discrete nanoparticles. In the case of silver, metal prefers also the PS domains, but upon repeated deposition and annealing the

formation of silver nanowires can be seen (**Figure 65e**), which have been found to display metallic conductivity.

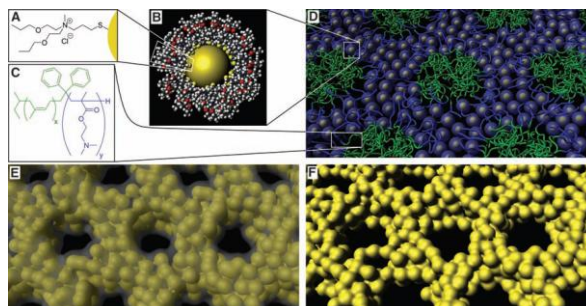


Figure 66 – 1.8-nm PtNPs (**B**) capped by a mercaptoammonium derivative (**A**) self-assemble in poly(isoprene-*block*-dimethylaminoethyl methacrylate) PI-*b*-PDMAEMA (**D**, PI in circular wire bundle and PDMAEMA in between the PI areas and amongst particles). Annealing affords a hybrid with an inverse hexagonal morphology (**E**) and pyrolysis produces a mesoporous Pt-C composite (**F**). Taken from Warren *et al.*^[26]

Warren *et al.* present results from the self-assembly of block copolymers with ligand-stabilized platinum nanoparticles, leading to lamellar and inverse hexagonal hybrid mesostructures with high nanoparticle loadings.^[26] Pyrolysis of the inverse hexagonal Pt/BCP hybrid produces an ordered mesoporous platinum-carbon nanocomposite with open and large pores ≥ 10 nm (**Figure 66E**). Removal of the carbon leads to ordered porous platinum mesostructures (**Figure 66F**). The platinum-carbon nanocomposite has very high electrical conductivity (400 S/cm) for an ordered mesoporous material fabricated from block copolymer self-assembly.

Wei and co-workers showed that pre-synthesized hydrophilic CdSeNPs and hydrophobic AuNPs ($\text{Au/C}_{12}\text{H}_{25}\text{-SH}$) can collectively self-organize in the two distinct blocks of a PS-*b*-P4VP diblock copolymer to form a highly ordered structure.^[27] At optimal concentrations of the CdSeNPs and AuNPs, the binding between the P4VP blocks and the CdSeNPs and the weak interactions between the PS blocks and the AuNPs led to dispersion of the two types of NPs in their respective P4VP and PS blocks and subsequent formation of a single-crystalline-like structure comprising P4VP/CdSe nanodomains situated at the apexes of the tetragonal cell and a matrix filled with the PS/Au NP network.

Sknepnek *et al.* considered nanoparticles and functionalized copolymers, block copolymers with attached end groups possessing a specific affinity for nanoparticles, in solution.^[28] Using molecular dynamics, they showed that nanoparticles are able to direct

the self-assembly of the polymer/nanoparticle composite. They studied a wide range of nanoparticle sizes and concentrations and showed that the nanoparticles order in a number of distinct phases: simple cubic, layered hexagonal, hexagonal columnar, gyroid, and a novel square columnar. They concluded that nanoparticles ordered with functionalized block copolymers can provide a simple and efficient tool for assembling novel materials with nanometer scale resolution.

4.2. Tuning the optical and electrical properties of AuNPs

4.2.1. Electro-optical properties

Nanoparticle-based materials have interesting optical and electrical properties, which are derived from the properties of the particles as well as their organization.

Müller *et al.* have shown that spherical gold nanoparticles behave optically like spheroidal gold nanoparticles when embedded in anisotropic materials. Choosing an electro-optically active medium such as a liquid crystal allows one to electrically tune the resonances by the application of an electric field.^[29]

Reznikov *et al.* observed that dispersing low concentrations of submicron ferroelectric particles in a nematic LC host enhances the dielectric response and induces a linear response to the electric vector $\mathbf{E}$ in a nematic. In contrast to molecular additives, these particle dispersions substantially lower the operating voltage of LC displays and related devices.^[30]

Schmid and Simon demonstrated that the synthesis and the organization of gold nanoparticles in 1–3 dimensions lead to unique electrical properties, caused by Coulomb charging and molecularly supported electron transfer.^[31] They insist on the fact that the complex interplay of particle size and size distribution, of constitution, symmetry, conformation of the ligand molecules, the state of charge of the particles, and of the embedding media and dielectric environment is not far enough understood. Therefore, the

electrical properties need to be studied further to prove the reliability of the design strategies they adopted.

AuNPs doped ferroelectric liquid crystal (FLC) mixture has been studied for its optical and electro-optical properties. Fivefold increase in optical tilt is obtained in the doped FLC case at an applied bias of mere 0.1 V. Moreover, adding of gold nanoparticles to FLC brings memory in the sample cell unlike the case of pure FLC. The enhanced intrinsic field created in the sample because of AuNPs is attributed to the high tilt and strong memory effect. The interaction of the collective electron wave oscillations in the AuNPs with the electromagnetic wave from the incident light traversing through FLC molecules probably leads out the observed results.^[32]

Evans *et al.* have studied the electro-optic response of a thin layer of liquid crystal deposited onto gold nanorods.^[33] For *p*-polarized light incident from the liquid crystal side, the extinction peak associated with the nanorod longitudinal plasmon resonance is completely suppressed. The peak could be recovered by applying an external electric field parallel to the long axis of the nanorods. No extinction peak suppression is observed when the light was incident from the nanorod side. The effect is explained by polarization properties of liquid crystal.

Kumar *et al.* have reported the synthesis of AuNPs fully covered with triphenylene (TP)-based discotic liquid crystal and their dispersion in a columnar matrix.^[34] Characterizations indicate the intercalation of TP-AuNPs into the matrix of discotic liquid particles. While a minor shift in the transition temperatures was observed, the nature of the mesophases is not disturbed in these composites. They also exhibit enhanced electrical conductivity of more than six orders of magnitude compared to the corresponding neat triphenylene.

Khoo and coworkers modeled theoretically and studied experimentally the optical properties of gold nanoparticles doped *n*-dodecane.^[35] The refractive indices that were measured exhibited resonances at visible wavelengths, which became more pronounced as the volume fraction of nanoparticles was increased. The measured spectra agreed well with the calculations based on simple Mie scattering theory. This preliminary study shows that gold nanoparticles dispersed in fluid media are interesting materials for certain metamaterial properties, including tenability of the refractive index when they are dispersed in appropriate birefringent media.

Khoo and co-workers also reported the dispersion of nanoparticles in a nematic liquid crystal host medium that provides an efficient way of designing tunable optical metamaterials responding from the visible to the terahertz and microwave regime. As studied in this article, these systems exhibit much larger birefringence than the nematic host and possess sub-unity, zero, and even negative refractive indices with unique reflection and transmission properties.^[36]

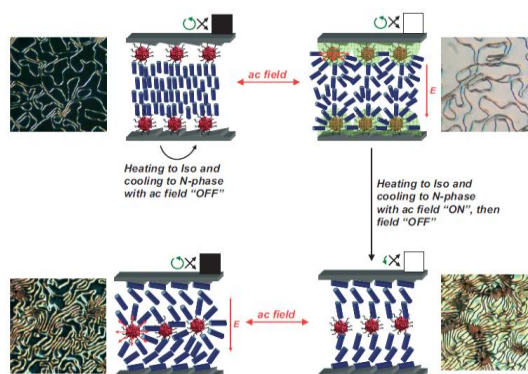


Figure 67 - Initial orientation and electric-field-driven reorientation of the N-LC molecules under cell preparation conditions, filled and cooled at field-OFF (upper section), and after heating above the clearing point and subsequent cooling to the N-phase at field-ON (lower section). Taken from Qi *et al.*^[37].

Hegmann and co-workers demonstrated an unprecedented dual alignment and switching mechanism in planar LC cells using nematic liquid crystal (N-LC) molecules (**Figure 67**) with dielectric anisotropy $\Delta\epsilon > 0$ and small amounts of alkyl thiolate-capped gold nanoclusters.^[37] In both thermal- and field-history-dependent modes, the threshold voltages were lower and the dielectric constants were higher than the values obtained for the pure N-LCs.

Electron hopping in films of nanoparticle-cored dendrimers (NCDs) including 60 % of n^{th} -generation dendrons ($[G_n]_{60\%}$ NCDs) was investigated by Shon and co-workers by measurements of the current-potential response of NCD films on interdigitated array electrodes.^[38] Different slopes of current-potential responses suggested that the resistance of NCD films increases with increasing generation of dendrons in the monolayer surrounding a nanoparticle core. They suggested that this is probably due to the larger nanoparticle core edge-edge distance of $[G_3]_{60\%}$ NCDs, resulting in slower electron hopping through the films. Consequently, the resistance of films prepared from $[G_2]_{60\%}$ NCDs was higher than that of films from $[G_1]_{60\%}$ NCDs. These results suggest that the

electronic properties of monolayer-protected nanoparticles can be further controlled by surrounding the nanoparticle with dendrons of different generations.

4.2.2. About metamaterials

The original idea of this project was to prepare organic-inorganic composite materials which exhibit a negative index of refraction (**Figure 68**). These are the so-called metamaterials (MM). A promising concept for the elaboration of metamaterials is the use of periodic structures with periods considerably shorter than the wavelength of light.^[39]

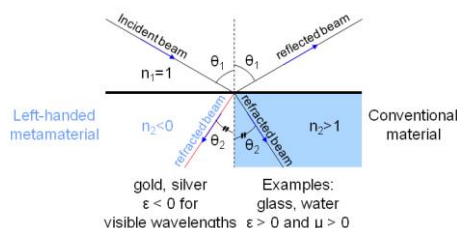


Figure 68 – For a negative refractive index material the refracted beam occurs on the same side of the surface normal as the incident beam following Snell's law $n_1 \sin \theta_1 = n_2 \sin \theta_2$, with $n_2 < 0$.

Metamaterials are known for the microwave regime of the electromagnetic spectrum,^[40] for which the necessary structuring of matter can be obtained by a top-down approach. Extension towards the infrared and visible regions requires structuring at the dimensions that are beyond the practical limits of the top-down approach. This is the reason why, to overcome this problem, a bottom-up strategy was adopted for the preparation of metamaterials operating in the visible.^[35, 41] One way to perform that is the organization of metal particles by incorporating them into liquid-crystalline matrices, i.e. randomly dispersing coated core-shell NPs in a LC^[36, 42] or well-defined nanoparticles containing a metal core and LC ligand shell.^[43, 44]

Rockstuhl and Scharf emphasized the fact that a potential realization of such arrangements can be envisaged by incorporating nanoparticles in mesogenic dendritic molecules and presented an analysis of the optical properties of a MM based on closely spaced metallic nanoparticles of small sizes.^[45] The properties of such a medium allow the effective permittivity to take negative values in the spectral domain. They discussed the influences of the period and the inter-plane distances, and both parameters influence on the effective permittivity.

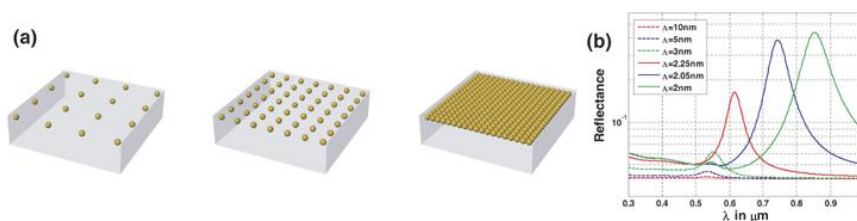


Figure 69 – Metamaterial (MM) design: It consists of a monolayer of periodically arranged gold nanoparticles (diameter $D = 2$ nm) embedded in an organic host medium as a function of the length of the square period. The closer the particles are (a), the stronger the reflectance is (b). Taken from Rockstuhl and Scharf.^[45]

Typical inter-layer distances in such a concept are about 5 nm, whereas the intra-layer spacing is given by the size of the molecule.^[46] With the results obtained, it can be stated that the resonant behavior of the unit cell still plays an important role at a particle size of 2 nm (**Figure 69**), which is a prerequisite for an effective MM.

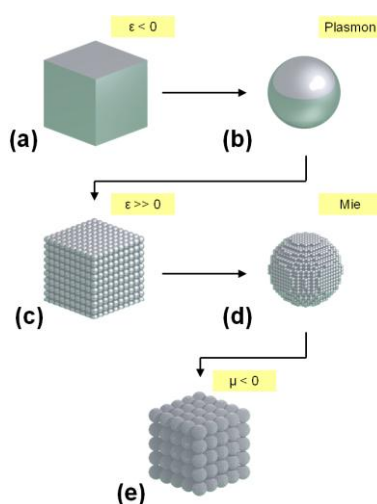


Figure 70 – Sketch of the steps to build an artificial meta-metamaterial. Using a noble metal such as gold provides a large negative real part of the permittivity ($\epsilon < 0$; part (a)) and nanoparticles made of it support localized surface plasmons (LSP) for appropriate wavelengths (part (b)). If a metamaterial (MM) is made of these nanoparticles, it becomes an effective medium having a strong Lorentz-type resonance in the permittivity around the LSP wavelength ($\epsilon \gg 0$; part (c)). In case the previous MM could be shaped as a sphere it will support strong Mie resonances (part (d)). Finally a material designed from these closely packed MM spheres gives a meta-metamaterial (MMM) with a strong negative permeability in a domain slightly smaller than the wavelength of the Mie resonance ($\mu < 0$; part (e)). Taken and adapted from Rockstuhl *et al.*^[44]

The concept to access artificial three-dimensional structure is to build unit cells (nanoparticles) surrounded by an organizing media (liquid-crystalline dendrimer coating) controlling the spatial arrangement by self-assembly with well ordered and controlled

arrays of nanoparticles (illustrative sketch in **Figure 70**). They consequently benefit from a Lorentz-type resonance in the permittivity at the collective plasmon frequency and may produce resonances in the permeability possibly leading to negative refractive indices (**Figure 68**).^[44, 45]

4.3. Results and discussion

4.3.1. Marangoni instabilities observations

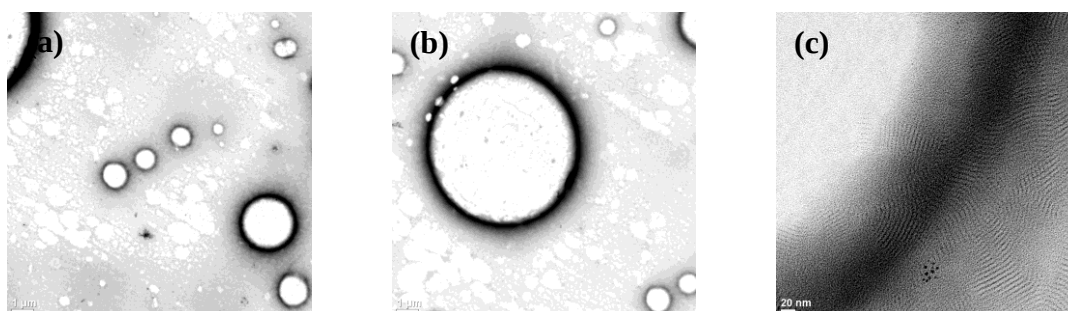


Figure 71 – Rings of particles resulting from Marangoni instabilities concomitant with the rapid evaporation of CH_2Cl_2 solution of particles **A** ($\text{Au/G}_1\text{CB-SH}$). Images (a) and (b) show the different sizes of rings: from a few tenth of nm to several μm . Image (c) magnifies the rim of a ring and shows that rows of particles are particularly emphasized close to it.

After synthesis and purification, a drop of particles is deposited on a carbon-coated copper grid placed on a filter paper. The solvent is left to evaporate under the hood under the cover of a watch glass without heating and subsequent TEM observations are made. First observation at low magnification revealed the formation of rings of particles of various sizes (**Figure 71**). The latter may result from a very thin film and/or a very low interfacial tension leading to long wavelength Marangoni instabilities;^[47] this appears when the film thickness is of the same range as the convection fluxes (**Figure 57**, left). A long-range deformation of the surface is then generated and lead to the film rupture by a hole nucleation process (**Figure 57**, right).^[48] This is obtained whatever the capping ligand of NPs (**Figure 72** and **Figure 73**).

More complex organizations made of close-packed structures are observed on the TEM grid. Arrays of polygonal patterns (**Figure 72**, e and f) and/or chaotic pictures (**Figure 73**) are seen. These structural changes are seemingly independent of the solvent used (low polar but volatile CH_2Cl_2 vs. polar MeOH) even if they depend on the evaporation rate (provided that the evaporation is fast enough) and thus may be due to the increase in nanoparticle concentration and appeared to be independent of magnetic dipolar interactions as well as shape-independent as demonstrated by Pileni *et al.*^[10]

An interesting point to notice is the assembly of particles inside and at a close proximity of the ring boundaries. Even if none of the sample presented here is monodisperse, particles bearing the $\text{G}_1\text{CB-SH}$ dendron present a distinct organization on the surface (**Figure 71** and **Figure 73**) at the opposite of the particles capped by ‘simple’ thioalkane chains (**Figure 72**).

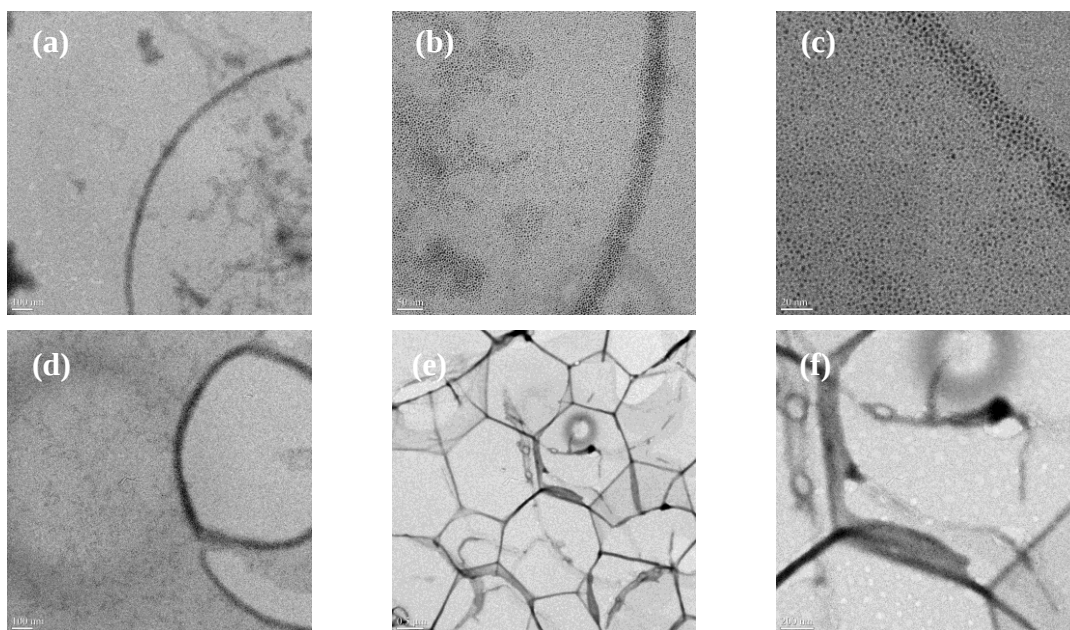


Figure 72 – Rings of AuNPs capped with $\text{C}_{12}\text{H}_{25}\text{-SH}$ (a and b), pMP (c), $\text{C}_{10}\text{H}_{21}\text{-SH}$ (d) and $\text{C}_6\text{H}_{13}\text{-SH}$ (e and f) deposited from a CH_2Cl_2 solution (c: from methanol) on a carbon-coated copper grid. It can be noticed that no particular organization of particles is observed close to the ring rim as it was the case for particles **A** in **Figure 71**. Note a deformation of the rings in the case of $\text{Au/C}_{10}\text{H}_{21}\text{-SH}$ (d) and even the observation of polygon-shaped patterns (a penta-, a hexa-, and a heptagone can be noticed in the middle of (e)) magnified in (f).

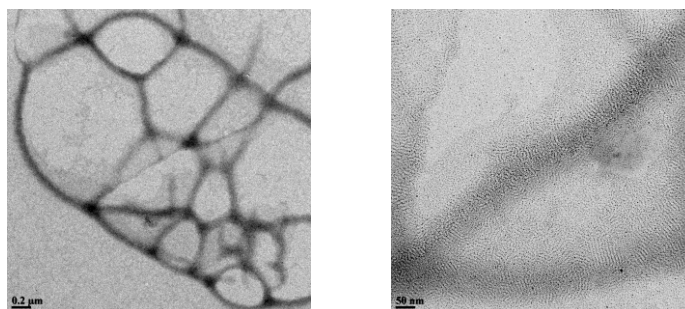
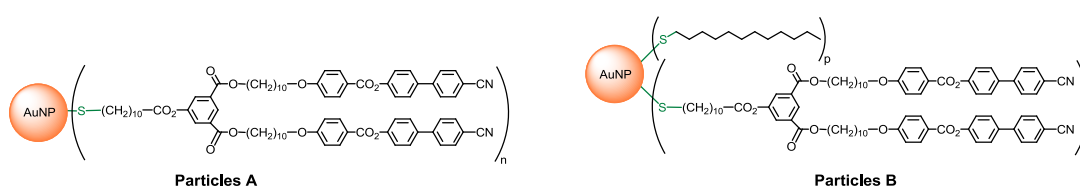


Figure 73 – Cross-linked rings resulting from the evaporation of CH_2Cl_2 of a solution of gold particles containing $\text{G}_1\text{CB-SH}$ introduced by ligand exchange on $\text{C}_{12}\text{H}_{25}\text{-SH}$ -capped particles ($\text{Au/C}_{12}\text{H}_{25}\text{-SH} \pm \text{G}_1\text{CB-SH}$). The dark “walls” correspond to nanoparticles aggregates, whereas the bright regions correspond to low particle density areas.

4.3.2. AuNPs bearing different ratios of $\text{G}_1\text{CB-SH}$

Some of these results concerning the AuNP organization are published in *Helv. Chim. Acta*, 2008.^[49] In addition, illustrative TEM images are added in the present manuscript to emphasize this interesting phenomenon.

AuNPs particles including compound **1** ($\text{G}_1\text{CB-SH}$) in their shell were synthesized in two different manners: the first one lead to particles **A** in a direct synthesis where compound **1** is directly used as the stabilizing ligand; the second one results from a ligand exchange with compound **1** on $\text{Au/C}_{12}\text{H}_{25}\text{-SH}$ synthesized prior to this (**Scheme 19**).



Scheme 19 – AuNPs **A** including 100 % of compound **1** and AuNPs **B** having 40 % of cyanobiphenyl derivative **1**.

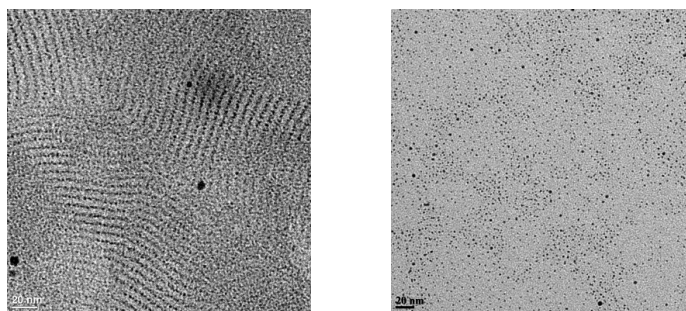


Figure 74 - TEM micrographs showing rows of 1.2-nm gold nanoparticles **A** (left) and 1.7-nm nanoparticles **B** (right). Depending on the ratio of the mesogenic ligand present in the particle shell, organization of particles is observed (100 % covering for AuNPs **A** and about 40 % for AuNPs **B**).

Compound **1** attached to gold nanoparticles (**Scheme 19**) promoted an organization on the surface of carbon-coated copper grids: the particles arrange in evenly spaced rows (**Figure 74** left, **Figure 75** and **Figure 76**). In this organization, the particle cores within one row are closely packed, and separated from each other by less than 1 nm. The separation between the rows is *ca.* 6.5 nm, which corresponds to 1.3 times the length of compound **1** ($L = 5.3$ nm) in its fully extended conformation. This can be interpreted as the formation of layers, as for smectic phases, with interdigitation of the cyanobiphenyl mesogenic units from one layer to the adjacent one.

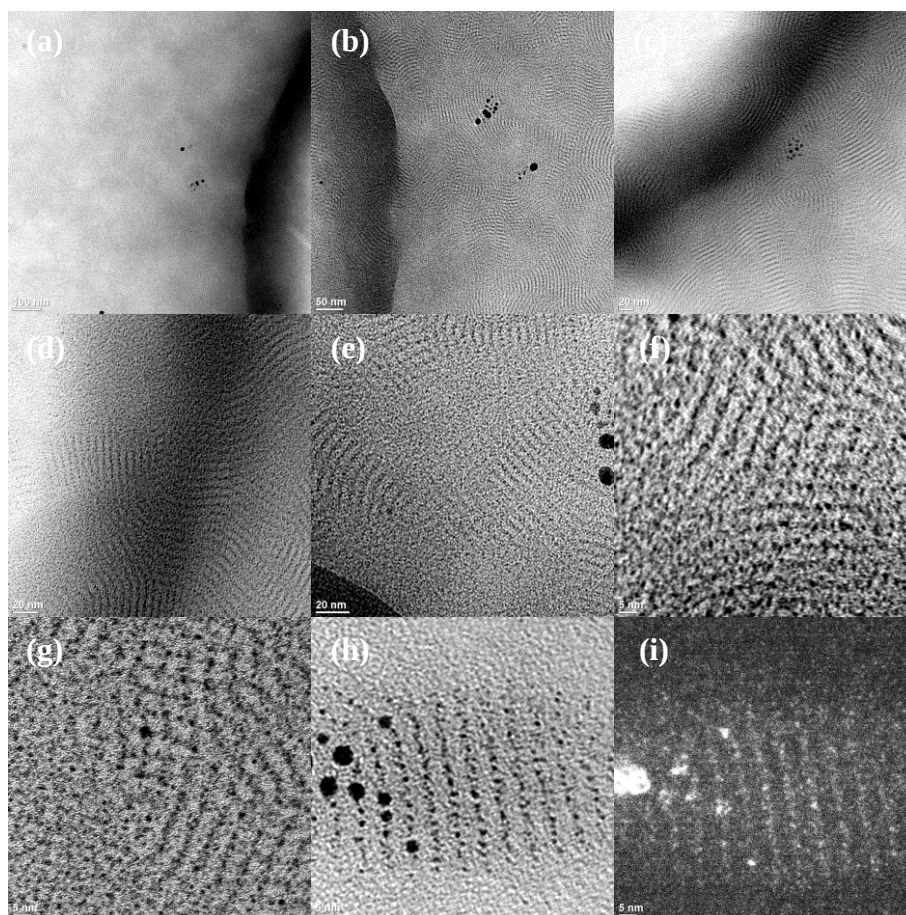


Figure 75 – TEM images corresponding to the particles **A** sample (Au/G₁CB-SH). The observation area is located close to a ring of high particle density (a), vast areas of evenly arranged small AuNPs (b-e), bigger particles are however present in the sample (a-c, e, h) resulting from the direct synthesis with G₁CB-SH. Detailed areas from (e) are given in (f) and (g). (h) (and its corresponding dark field (i)) corresponds to a different area farther from the ring and it is noticeable that bigger particles are aligned in the small particle rows as well.

Interestingly, decreasing the dendrimer loading on the gold particle surface from 100 to 40% results in a less pronounced organization (**Figure 73**) or even in a complete loss of organization (**Figure 74**, right). For 100 % coverage, all the observed areas without exception present organized particles, while in the case G₁CB-SH is present in a lesser extent fewer areas of arranged particles are visible.

Thus, compound **1** acts as a self-assembly promoter of gold particles, provided that sufficient loading is reached.

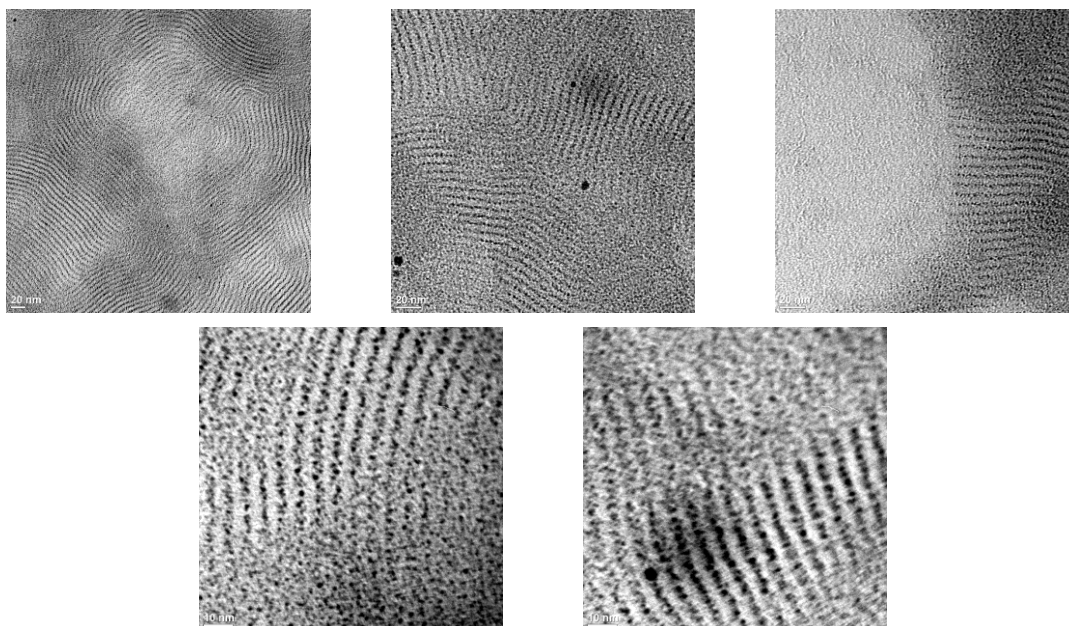
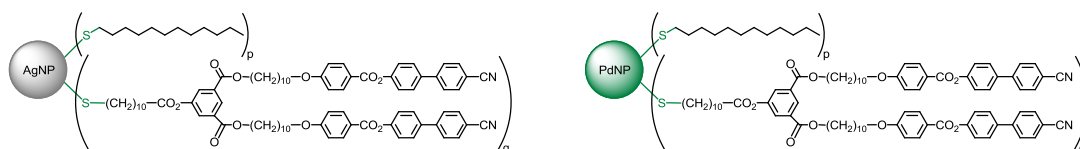


Figure 76 - Au/G₁CB-SH particles resulting from a batch different from those presented in **Figure 75**. The same protocol leads to the same observations (concerning the organization of particles).

Another synthesis of particles **A** was made and the organization of particles is still present when observed at TEM (**Figure 76**). Although the synthesis is reproducible, a few considerably larger particles are still present; it denotes the rather loose control of G₁CB-SH in stabilizing all the particles in a similar manner during the passivation/growth mechanism. This is probably due to a relative large steric hindrance of the ligand resulting in a lesser mobility than in the case of R-SH ligands for example.

4.3.3. Assembly of silver and palladium nanoparticles

In a similar manner to the previous study on gold (§ 4.3.2),^[49] silver (AgNPs) and palladium nanoparticles (PdNPs) were synthesized. The procedure followed a modified protocol described by Zheng *et al.*^[50] followed by a ligand place exchange with compound **1** to form particles **F** (Ag/C₁₂H₂₅-SH±G₁CB-SH) and particles **G** (Pd/C₁₂H₂₅-SH±G₁CB-SH) (**Scheme 20** left and right respectively). These particles are described in the previous chapter (paragraph 3.4.1) and the synthesis is detailed in the Second appendix.



Scheme 20 – $C_{12}H_{25}-SH$ -coated AgNPs and PdNPs were subjected to ligand exchange reaction with the thiolated cyanobiphenyl derivative **1** leading to NPs **G** ($Ag/C_{12}H_{25}-SH \pm G_1CB-SH$) and NPs **H** ($Pd/C_{12}H_{25}-SH \pm G_1CB-SH$).

The AgNPs and PdNPs synthesized here were made to compare the influence of metal on the final particles, the validation of the possibility to introduce dendrimers in other metallic NPs shell and finally to check the induction of organization by the latter. Therefore the results presented here for silver and palladium were not deeply studied (the main topic being gold), the synthesis conditions were not optimized and as consequence a broad size distribution can be noted especially for AgNPs (**Figure 77**).

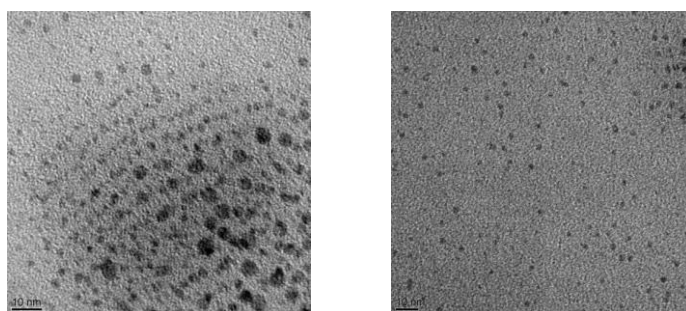


Figure 77 – TEM micrographs of particles **F** ($Ag/C_{12}H_{25}-SH \pm G_1CB-SH$). Left: depending on the observed area an organization of AgNPs is observed even for a large distribution of particle sizes. Right: a different area of the same sample where organization is lost and randomly located particles on the surface are of uniform size distribution.

Even if some bigger particles are present in the sample (**Figure 77**) and the size distribution for AgNPs is relatively large the mean diameter is about 1.6 ± 0.7 nm (the mean diameter is 1.4 ± 0.4 for the image on the right). 1H -NMR spectrum revealed the presence of the dendron tethered to silver in the proportion of about 4 % with respect to the $C_{12}H_{25}-SH$. The rows of particles are separated by 6.2 nm on average and each particle in a row is separated by about 2 nm but this determination is not very precise due to the broad size dispersity of particles and its consequences: particle lines are broken leading to the deformation of the particle arrays in the best case and disappearance in the worst ones.

The PdNPs sample has a narrow size distribution and presents more organization than the silver one (**Figure 78**). The mean diameter is 1.46 ± 0.47 nm, the particles are separated by 3.5 nm each other in a row and rows are separated from 7.5 nm.

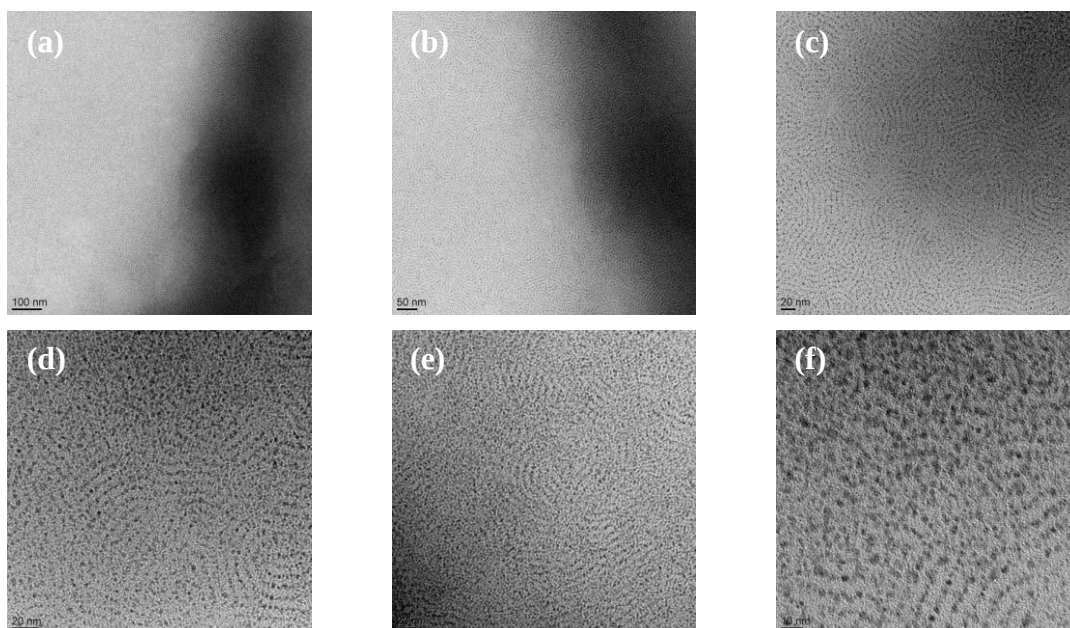
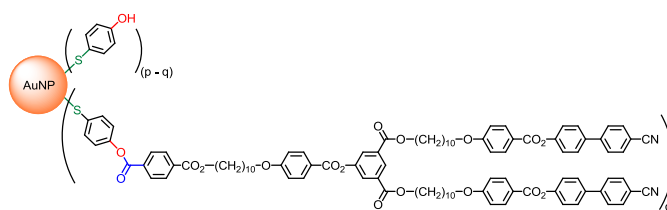


Figure 78 – TEM micrographs of particles **H** ($\text{Pd/C}_{12}\text{H}_{25}\text{-SH}\pm\text{G}_1\text{CB-SH}$). Samples from (a) to (f) show the surface organization of PdNPs at different magnifications. One can notice the fingerprint-like structures that PdNPs form.

4.3.4. Organization of AuNPs resulting from esterification

Particles prepared by esterification of dendrons on AuNPs (Boudon *et al.*^[51]) revealed a one-dimensional organization of particles like the one described above (§ 4.3.2) in the case of direct synthesis or ligand exchange reaction with compound **1** ($\text{G}_1\text{CB-SH}$). The cyanobiphenyl dendron is analogous to compound **1** but the thiol group of which was replaced with a terminal benzoic acid allowing an esterification reaction with AuNPs surrounding $-\text{OH}$ groups. This was done with compound **4** leading to esterified particles **C** (**Scheme 21**), the presentation of which was given in paragraph 3.4.2.



Scheme 21 – Structure of AuNPs (Au/pMP} $\}$ G₁CB–COOH). Even if the exact proportion of esterified could not be determined ¹H-NMR revealed underlying signals below the broadened one of the G₁CB–COOH (cf. paragraph 3.4.2 for explanations).

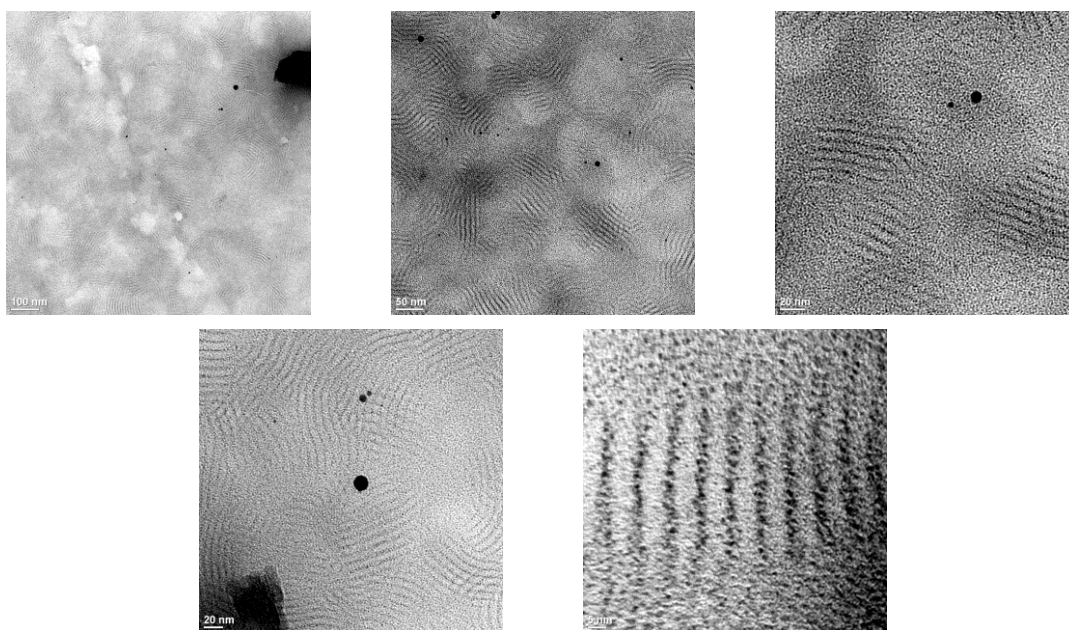


Figure 79 – TEM micrographs of esterified AuNPs (Au/pMP} $\}$ G₁CB–COOH) presented in paragraph 3.4.2 showing partial area of organized particles and some considerably larger particles and aggregates. These particles result from an equimolar incoming amount of compound **4** (G₁CB–COOH) with respect the ligands to esterify.

To synthesize these particles an equivalent amount of dendrons was introduced corresponding to the number of ligand per particles; i.e. about 80 pMP ligand per particle (see previous chapter) and as a consequence 80 equivalents were used with respect to the gold particle amount (**Figure 79**).

Decreasing the incoming loading of dendrons to 40 % lead to the particles observed in the previous chapter (paragraph 3.4.2, particles **D** and compound **4**, Au/pMP} $\}$ G₁CB–COOH). Nevertheless a minimum amount of dendrons are required otherwise particle organization at the nanoscale is lost (**Figure 80**).

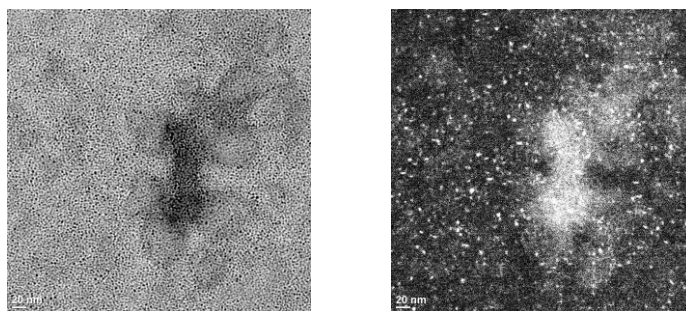


Figure 80 – TEM micrographs of esterified AuNPs (Au/pMP}G1CB-COOH) synthesized from an incoming dendron ratio of 40 % of the pMP.

Once again in the particular case of esterification of dendrons on AuNPs, the dendron used (compound **4**, G₁CB-COOH) acts as a self-assembly promoter provided a sufficient amount is present in the particle shell.

4.3.5. Scope and limitations

Many attempts were done with other dendron types and size (generation) but this first-generation cyanobiphenyl derivative was the only one that organized particles. It worked in the case of gold, silver and palladium, when used as a thiolated derivative in direct or exchange reaction and as a carboxylic acid derivative for esterification on AuNPs. One can notice that in the presented results, the length of the dendrons in their fully extended conformation is about four times the diameter of the particles they capped (i.e. an organic layer eight times larger than the gold core); the steric hindrance was high enough to promote organization (compared to G₀ mesogenic derivatives) and low enough to maintain a certain flexibility in the system.

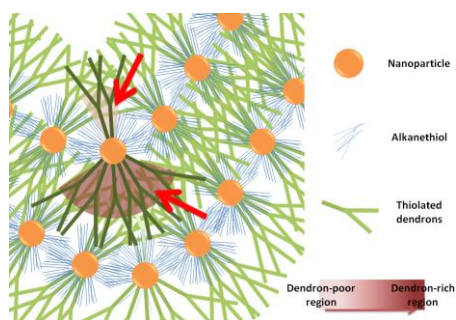


Figure 81 – Sketch of a supposed orientation of the dendrons on the surface of particles. The arrows indicate the dendron-rich and dendron-poor regions of the particles that are possibly at the origin of the straight organization rupture.

In addition, the dendron morphology favors π - π stacking of the cyanobiphenyl units, which can result in the formation of layers, as for smectic phases, with interdigitation of the mesogenic units from one layer to the adjacent one.

The flexibility of the system allows for reorientation of the mesogenic parts inside the organic shell. Thus in the evenly spaced rows of particles presented in the case of gold, nearly perfectly straight lines were observed (**Figure 74**). But when present in less proportion (**Figure 78**) the lines become curved. It could result from the reorientation of a part of the dendrons directed predominantly on one side of the particle, the other ones in minor proportion pointing to the opposite direction. As a result, the lines of particles are curved because of a greater steric bulk on one side of the particle. An illustrative sketch is given in **Figure 81**.

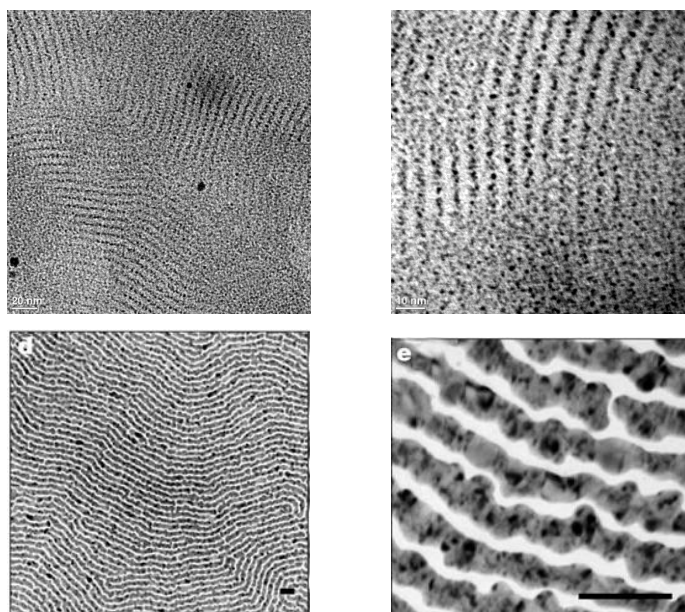


Figure 82 – Both images on top are from the synthesized Au/G₁CB-SH and display fingerprint-like structures just like in the images at the bottom (d and e, taken from Lopes and Jaeger^[25]), where the particles organization is mediated by block copolymers.

One can notice the similarities between the organization displayed by our particles including liquid-crystalline dendrimers in their shell (Au/G₁CB-SH) and particles organized within block copolymers. The main advantage in our case is the scale of the organization: for dendrimers-base AuNPs, the space between stripes is about 5 nm whereas for the block copolymer assembly it is about 50 nm. This 10-fold factor could allow us to preserve the optical properties described by Rockstuhl and Scharf^[45] for 3D assemblies that are completely wiped out beyond 10 nm.

When all the samples including compound **1** are compared the same organization type is observed (**Figure 74**, **Figure 75**, **Figure 76**, **Figure 77**, **Figure 78** and **Figure 79**) independently of the metal used and of the proportion of it (unless below a critical level). Obviously a limitation to this comparison is the size of particles: despite they are not the same, they are all in the same range. Indeed 1.2-1.6 nm is between one third and one fourth of the G₁CB-SH dendron length in its extended conformation (5.3 nm). It means that the gold core is included in a relatively large protective organic shell.

As the inorganic parts are concerned, replacing gold with silver or palladium amounts to a core of about a half weight. Such a system where the ratio of organic to metal of less atomic weight, is undoubtedly favorable for organization under the appropriate conditions. No doubt that this also has consequences on the kinetics of the final system for the formation of ordered phases on a macroscopic scale under a temperature gradient. All the mesomorphic gold samples correspond to the smallest particles. However no liquid crystalline behavior was observed in the cases of silver and palladium, probably because the LC proportion was not high enough to induce a mesophase.

As a matter of fact compounds **1** acts as a self-assembly promoter for the formation of NP arrays. Provided it is present in sufficient amount in the particle shell, one-dimensional arrangements were successfully observed. Indeed a random arrangement of nanoparticles within one layer suggests the lack of a long-range ordering. More monodisperse samples and subsequent SAXS characterization (it has sense only in this case) would be interesting to be performed for a better comprehension of the key parameters. Monodisperse systems have proven to lead easily to hexagonal 2D arrangements^[10, 21, 22, 52-54] which is the first step towards the formation of 3D materials with the presented properties (paragraph 4.2).^[44]

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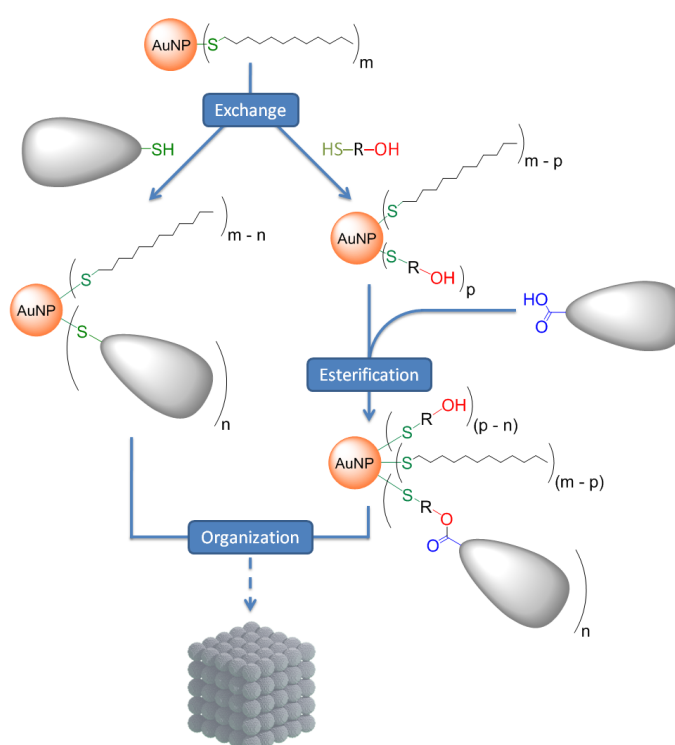
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5. Conclusions and outlook

5.1. General conclusion

In this study, liquid-crystalline-dendrimer-based gold nanoparticles (Au/LCDs) have been successfully prepared by ligand exchange or esterification and depending on the nature and the proportion of the grafted dendrons; they exhibit either mesomorphic properties or a self-organization behavior on surfaces at the nanometer scale.

Concerning the synthesis, three different pathways have been used to access these new materials: the first and simplest one consists in the direct synthesis of AuNPs using thiolated dendrons by the convenient Brust's biphasic method;^[1] the second one, using the same synthetic method, starts from dodecanethiol-stabilized AuNPs (Au/C₁₂H₂₅-SH); the third way begins with the synthesis of 4-mercaptophenol-stabilized AuNPs (Au/pMP) according to Brust's monophasic method.^[2]



Scheme 22 – Summarizing diagram of both pathways adopted to tether dendrons on AuNPs starting from Au/C₁₂H₂₅-SH that could possibly lead to metamaterials via a three-dimensional organization. The grey lobes represent dendrons, and for ω -hydroxythiols **R** represents an alkyl or a polyethylene glycolalkyl.

The second pathway has led to Au/LCD either by (A) a simple ligand exchange with thiolated dendrons on Au/C₁₂H₂₅-SH, or (B) by introducing first the -OH moiety by ligand exchange reaction on Au/C₁₂H₂₅-SH and secondly performing an esterification of the HOOC-dendrons on the latter NPs (see **Scheme 22**). The third pathway has allowed the direct esterification of HOOC-dendrons on Au/pMP.

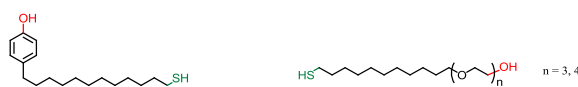
Any of these approaches has its advantages and drawbacks. The direct synthesis has been achieved in one single step but required a large quantity of dendrimers. The ligand exchange allowed size-controlled particles as well as a relatively good control over the amount of exchanged dendrimer, however this strategy also required an excess of dendrimer. Finally the esterification of dendrons has appeared to be easy to carry out and has been the method which required the least amount of dendrimers; a default quantity has even allowed one to esterify only a fraction of all the available functional groups. In addition, it has been shown that the esterification strategy can be applied successfully to graft the G₀-mesogen up to G₂-dendrimer onto AuNPs. On the other hand, size exclusion chromatography has been used as an effective purification in the early stages of Au/LCDs syntheses (precursor particle synthesis and ligand exchange) and ultrafiltration in a stirred cell has been found as the fastest and simplest way to yield high purity final dendrimer-based materials.

Concerning the characterization of these particles, a G₀ chiral mesogen as well as a first-generation cyanobiphenyl derivative esterified on Au/pMP have given rise to non-characteristic mesophases. Besides, TEM observations revealed that the first-generation cyanobiphenyl derivative has been able to promote self-organization on a surface when used in a direct synthesis or in an exchange reaction on Au/C₁₂H₂₅-SH, by esterification on Au/pMP, and in an exchange reaction on Ag/C₁₂H₂₅-SH and Pd/C₁₂H₂₅-SH, although no liquid-crystalline phase was observed for any of these compounds using polarized optical microscopy.

In conclusion, this study has emphasized esterification (in addition to direct synthesis and ligand exchange) as a valuable means to graft liquid-crystalline dendrimers to the shell of small particles with a low polydispersity. Even though only surface organization promoted by dendrons was observed so far, an optimization of synthetic parameters as well as the tuning of the LCDs could undoubtedly allow a better organization and the opportunity to access our aim, metamaterials with their outstanding properties.^[3-10]

5.2. Outlook

First and foremost the method which seems the best suited for the purification and separation of particles is based on the size (molecular weight). Regrettably very few devices exist for apolar organic solvents such as toluene, dichloromethane or more polar such as THF. While some separation membranes works fine with these solvents, the membrane support are not chemically compatible! So there is food for thought in this area.



Scheme 23 – Chemical structures of thiol derivatives of interest for nanoparticle synthesis. Left is 4-mercaptododecylphenol (4-mdp)^[11] and on the right are (11-mercaptoundecyl)tri-(or tetra-)ethylene glycol.^[12]

Then comes the question of thiol ligands for the synthesis of particles. Many of them are commercial and not very expensive (e.g. dodecanethiol). But the synthesis of new optimized particles requires the synthesis of tuned ligands. In this context we tested the synthesis of some ligands^[11, 12] (**Scheme 23**) but regarding the low yield obtained and the time spent, their commercial version was preferred when available (this is not the case of the first compound in **Scheme 23**). The synthesis of new thiolated ligands appears necessary.^[13-17]

Moreover, even if the approach of the esterification for the preparation of these dendrimer-based nanoparticles is attractive, other ways of coupling have to be investigated or further developed, for example: the very popular “click chemistry,”^[18-25] Sonogashira cross coupling,^[26] or Grignard reaction.^[27]

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Appendices

First appendix

Generalities

Size exclusion chromatography (also known as gel filtration for a hydrophilic medium and gel permeation chromatography for a hydrophobic one) is a powerful chromatographic method based on the separation of analytes according to their size, that is to say hydrodynamic volume under low pressure. With this technique high molecular weight compounds are easily separated from low molecular weight ones. The stationary phase is generally composed of small ($\sim 10\ \mu\text{m}$) beads made from polymers (polyacrylamide, dextran, agarose, silica, polystyrene, etc.) containing a network of channels and uniform pores in which solvent and solutes diffuse. Molecules bigger than the mean pore size are excluded and they elute almost at the speed of the mobile phase. Smaller molecules going inside the pores are literally trapped and extracted from the mobile phase during a relatively long period and they are consequently eluted later than the bigger ones. Between small and big, intermediate-size molecules are more retained according to their diameter and shape.

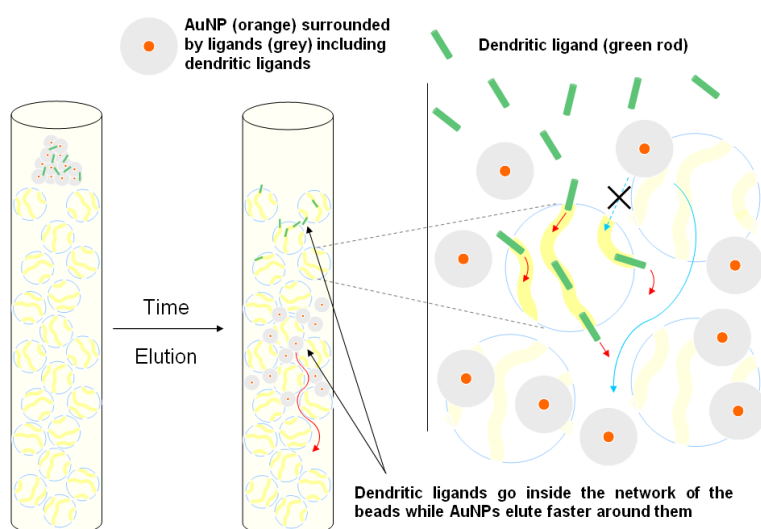


Figure 83 – graphical scheme for size exclusion chromatography.

One of the main advantages of this technique is the absence of physical or chemical interaction between analytes and the stationary phase. Indeed, these interactions would considerably decrease the efficiency of such a chromatography column and furthermore avoid sample loss which is not generally the case with other chromatographic techniques. Other advantages are the short and well-defined separation times, a relatively good sensitivity with narrow bands even if the resolution is limited to molecular masses with a difference of at least 10% as the major drawback.

Sephadex LH-20

Sephadex LH-20 is prepared by hydroxypropylation of Sephadex G-25, a bead-formed dextran medium. It has been specifically developed for gel permeation of natural products in organic solvents but its application has been extended to the separation of nanoparticles from the remaining free ligands used to protect their surfaces. Technical information on the handling of this gel permeation medium is provided by GE Healthcare.⁴

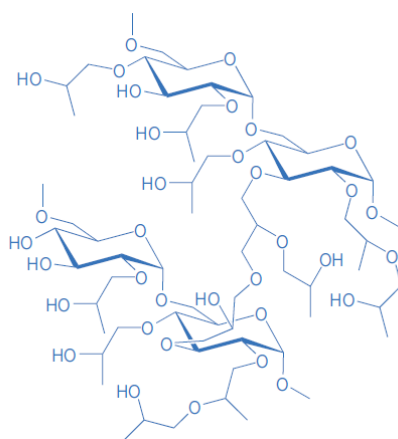


Figure 84 – Partial structure of Sephadex LH-20. The medium is based on hydroxypropylated dextran that has been cross-linked to yield a polysaccharide network.⁵

This resin was generally used to perform a further purification of particles (after washing steps over filtration membrane following the reaction) from free ligands rather than size separation as the molecular weight cut-off of $4000\text{--}5000\text{ g.mol}^{-1}$ is low considering the high molecular weight of metal particles.

⁴ Information come from GE Healthcare website: packing, preparation of sample, regeneration and storage are described in this document ([link to the pdf document](#)).

⁵ Information from GE Healthcare website: Data on Sephadex LH-20 ([link to the pdf document](#)).

Bio-Rad Bio-Beads SX-1

Bio-Beads S-X beads are a series of porous crosslinked polystyrene polymers used for gel permeation separations of lipophilic polymers and low molecular weight, hydrophobic materials in the presence of organic solvents. These nonaqueous spherical beads are used in much the same way aqueous gels are used, except that they are swollen with organic solvents during the separation.

Bio-Beads S-X1 beads are neutral, porous styrene divinylbenzene copolymer beads. It has exclusion limits from 600 to 14,000 daltons. This range makes it particularly suitable for the fractionation and separation of low molecular weight organic polymers and other hydrophobic substances. The amount of divinylbenzene crosslinkage determines the pore size, and hence the molecular weight exclusion limit of this gel. The beads have a crosslinkage of 1 %. Pore dimensions and exclusion limits are also influenced by the eluent employed; maximal expansion of the matrix is achieved with relatively nonpolar, aromatic solvents. The beads are typically used with toluene, methylene chloride, THF and mixtures of solvents. These organic solvents allow maximal swelling of the beads. If polar solvents, such as water or methanol, are used, the Bio-Beads S-X beads will not swell, and the pore size will be minimal. The chosen solvent should be the one used for the separation, and the same as the solvent in which the sample is dissolved.

The solvents should be of highest quality available, and preferably redistilled if non-volatile matter is present in them. Some solvents, e.g. tetrahydrofuran, develop peroxides on standing in contact with air. Solvents should generally be degassed prior to use and protected from atmospheric contamination, to prevent later outgassing during the chromatographic run.

Bio-Beads S-X1 beads will swell considerably, and should be placed in at least six times the resin weight of solvent (w/w). The higher crosslinked resins will not swell as much, so they will not require as much elution solvent. The swelling should always be done in the presence of excess solvent to prevent the resin from drawing up all the solvent, and possibly not swelling fully.

More information is provided on Bio-Rad website: www.bio-rad.com.

Solvent Resistant Stirred Cells for Ultrafiltration and Filtration Applications

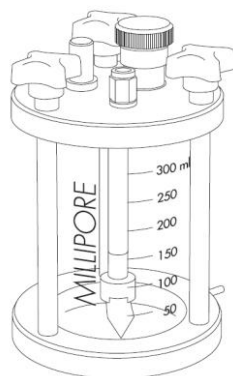


Figure 85 – Millipore ultrafiltration system: a separation membrane is set at the bottom of the cylinder and then the system operates with a N_2 pressure.

The Millipore Solvent Resistant Stirred Cell is constructed from stainless steel and borosilicate glass. It is designed to offer a rapid and efficient method for concentrating or desalting samples of up to 300 mL under high pressure.

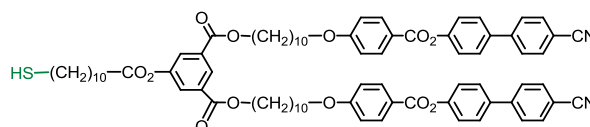
A solution is held over an ultrafiltration membrane in the pressurized cell. Solvent and solutes less than the membranes' molecular weight cutoff pass through the membrane as filtrate; solutes greater than the molecular weight cutoff are retained and concentrated within the cell.

The regenerated cellulose membranes were used with 10k or 30kDa molecular weight cut-offs.

More information is provided on Millipore's website: www.millipore.com.

Second appendix

Dendron characteristics used in this work



Compound 1 – 1st generation thiolated poly(aryl ester) dendron functionalized with mesomorphic cyanobiphenyl units.

Synthesis of compound 1. To a solution of first-generation HO-based dendron (the synthesis of which is reported elsewhere^[1]) (4.85 g, 4.45 mmol) and 11-mercaptoundecanoic acid (486 mg, 2.23 mmol) in dry CH₂Cl₂ (250 ml) at 0 °C was added 4-(dimethylamino)pyridinium toluene-para-sulfonate (DPTS) (655 mg, 2.23 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC) (2.30 g, 11.13 mmol), and 4-pyrrolidinopyridine (4-ppy) (spatula tip). The reaction mixture was stirred for 24 h at RT, and the solvent evaporated under vacuum. Purification of the crude material by column chromatography (silica gel 63-200 μm, CH₂Cl₂) and precipitation from CH₂Cl₂ with MeOH gave pure compound **1** (1.32 g, 46%).

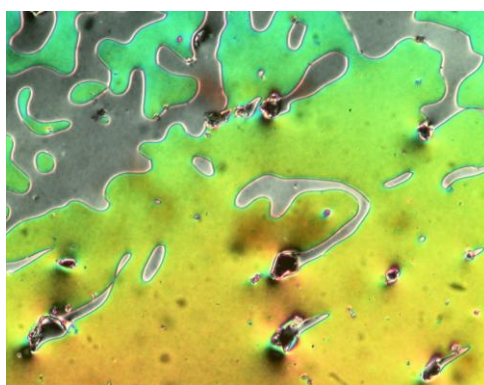
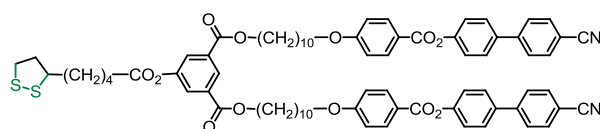


Figure 86 – Thermal-polarized optical micrograph of the texture displayed by **1**: in the nematic phase upon cooling the sample from the isotropic liquid to 173°C

Liquid-crystalline and thermal properties of compound 1: (investigated by POM and DSC) Dendron **1** gives rise to a smectic A phase in agreement with the nature of the

mesomorphic cyanobiphenyl units which tend to orient parallel one to each other, the consequence of which is the formation of layers^[1, 2] and an additional nematic phase is also obtained (texture are shown in **Figure 86**). Phase transition temperature T (in °C) and phase transition enthalpy changes (ΔH in kJ/mol) of compound **1**: T_g 17 SmA 162 (0.4) N. 175 (1.5) I.

NMR Data of compound 1: $^1\text{H-NMR}$ (400 MHz, CH_2Cl_2): 8.49 (*t*, 1 arom. H); 8.11 (*d*, 4 arom. H); 7.89 (*d*, 2 arom. H); 7.73 (*d*, 4 arom. H); 7.71 (*d*, 4 arom. H); 7.65 (*d*, 4 arom. H); 7.31 (*d*, 4 arom. H); 6.97 (*d*, 4 arom. H); 4.31 (*t*, 4H, CO_2CH_2); 4.03 (*t*, 4H, CH_2O); 2.57 (*t*, 2H, CH_2CO_2); 2.48 (*q*, 2H, CH_2SH); 1.83-1.69 (*m*, 12H, $\text{CO}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{O}$, $\text{CH}_2\text{CH}_2\text{CO}_2$, $\text{CH}_2\text{CH}_2\text{SH}$); 1.37-1.26 (*m*, 36 aliph. H). Anal. calc. for $\text{C}_{79}\text{H}_{88}\text{N}_2\text{O}_{12}\text{S}$ (1289.62): C 73.58, H 6.88, N 2.17, S 2.49; found: C 73.48, H 6.68, N 2.31, S 2.33.



Compound 2 – 1st generation poly(aryl ester) dendron functionalized with mesomorphic cyanobiphenyl units bearing a disulfide function.

Synthesis of compound 2: its preparation consists in the esterification of first-generation HO-based dendron (the synthesis of which is described elsewhere^[11]) with lipoic acid under standard reaction conditions according to the same procedure described for compound **1**, however 11-mercaptopundecanoic acid is replaced by lipoic acid.

NMR data of compound 2. $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2): 8.50 (*t*, 1 arom. H); 8.11 (*d*, 4 arom. H); 7.91 (*d*, 2 arom. H); 7.73 (*d*, 4 arom. H); 7.71 (*d*, 4 arom. H); 7.65 (*d*, 4 arom. H); 7.31 (*d*, 4 arom. H); 6.98 (*d*, 4 arom. H); 4.32 (*t*, 4H, CO_2CH_2); 4.03 (*t*, 4H, CH_2O); 3.62-3.55 (*m*, 1H, CH); 3.20-3.07 (*m*, 2H, SCH_2); 2.61 (*t*, 2H, CH_2CO_2); 2.49-2.41 (*m*, 1H, SCH_2CH_a); 1.95-1.88 (*m*, 1H, SCH_2CH_b); 1.82-1.68 (*m*, 12H, $\text{CO}_2\text{CH}_2\text{CH}_2$, $\text{CH}_2\text{CH}_2\text{CO}_2$, $\text{CH}_2\text{CH}_2\text{O}$, CHCH_2); 1.46-1.30 (*m*, 26 aliph. H). Anal. calc. for $\text{C}_{76}\text{H}_{80}\text{N}_2\text{O}_{12}\text{S}_2$ (1277.59): C 71.45, H 6.31, N 2.19, S 5.02; found: C 71.27, H 6.40, N 2.24, S 5.03.

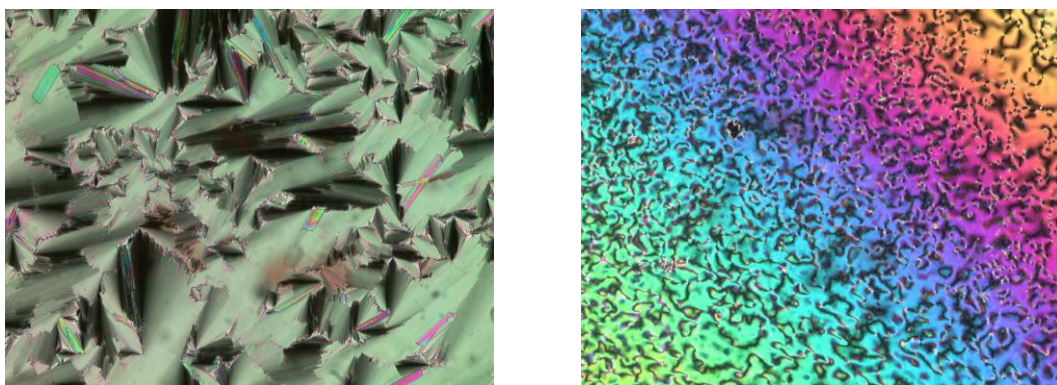
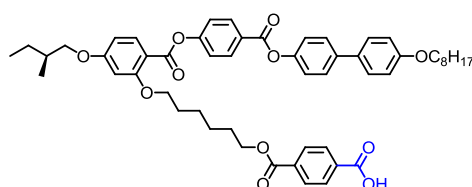


Figure 87 – Thermal-polarized optical micrograph of the texture displayed by **2**: in the smectic A phase (left) and in the nematic phase upon cooling the sample from the isotropic liquid (right)

Liquid-crystalline and thermal properties of compound 2: (investigated by POM and DSC) Dendron **2** gives rise to a smectic A phase in agreement with the nature of the mesomorphic cyanobiphenyl units which tend to orient parallel one to each other, the consequence of which is the formation of layers^[1, 2] and an additional nematic phase is also obtained (textures are shown in **Figure 87**). Phase transition temperature T (in °C) and phase transition enthalpy changes (ΔH in kJ/mol) of compound **2**: T_g 22 SmA 161 (0.1) N. 183 (1.6) I.



Compound 3 – Chiral mesogen bearing a carboxyl function

Name: (S)-4'-Octyloxybiphenyl-4-yl 4-{2-[6-(4-carboxybenzoyloxy)hexyloxy]-4-(2-methylbutoxy)benzoyloxy}benzoate

Synthesis of compound 3: To a 0°C CH₂Cl₂ solution (250 mL) of the alcoholic derivative^[3] (1.64 g; 2.26 mmol) and 4-carboxybenzaldehyde (0.34 g, 2.26 mmol), were added 4-(dimethylamino)pyridinium para-toluenesulfonate (DPTS) (0.67 g, 2.26 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC) (2.33 g, 11.31 mmol) and 4-pyrrolidinopyridine (4-ppy) (spatula tip). The solution was stirred during 24 hours at room temperature. Then the solvent was removed and the product was purified by chromatography column (CC; silica gel 63-200 μm) with CH₂Cl₂ giving pure compound **A2** as a white solid, yielding

72% (1.40 g, 1.63 mmol). To a solution of the aldehyde derivative **A2** (1.27 g, 1.48 mmol) in THF (60 mL) deionized water (12 mL), NaClO_2 (0.27 g, 2.96 mmol) and $\text{H}_2\text{NSO}_3\text{H}$ (0.29 g, 2.96 mmol) are added. The mixture was stirred during 4 hours at room temperature before THF was evaporated under reduced pressure and resulting aqueous solution was diluted into water (90 mL). The product was extracted with CH_2Cl_2 . Organic phases were gathered, dried over MgSO_4 , and evaporated to dryness under reduced pressure. The residue was dissolved in a minimum volume of CH_2Cl_2 , and then precipitation with methanol gave pure **Compound 3** as a white powder, yielding 82% (1.06 g; 1.21 mmol).

NMR Data of compound 3: ^1H -NMR (400 MHz, CD_2Cl_2): δ 8,24 (d, 2H, H_{arom}) ; 8,12-8,06 (m, 4H, H_{arom}) ; 7,99 (d, 1H, H_{arom}) ; 7,59 (d, 2H, H_{arom}) ; 7,52 (d, 2H, H_{arom}) ; 7,34 (d, 2H, H_{arom}) ; 7,24 (d, 2H, H_{arom}) ; 6,95 (d, 2H, H_{arom}) ; 6,57-6,53 (m, 2H, H_{arom}) ; 4,29 (t, 2H, $\text{CH}_2\text{O}_2\text{C}$) ; 4,07 et 3,98 (2t, 4H, OCH_2CH_2) ; 3,94-3,79 (m, 2H, CHCH_2O) ; 1,90-1,74 (m, 7H, CH et OCH_2CH_2) ; 1,62-1,28 (m, 16H, aliphatic chains +1 OH ?) ; 1,07 et 1,02 (2d, 3H, CHCH_3) ; 0,95 (t, 3H, $\text{CH}_3\text{CH}_2\text{CH}$) ; 0,88 (t, 3H, $\text{CH}_3\text{CH}_2\text{CH}_2$). MS (ESI, positive mode) for $\text{C}_{53}\text{H}_{60}\text{O}_{11}$ $[\text{M}+\text{Na}]^+$: 895.4.

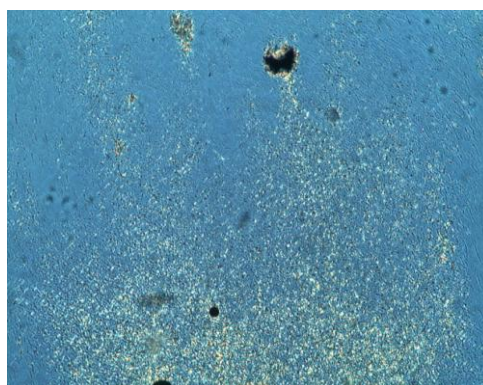
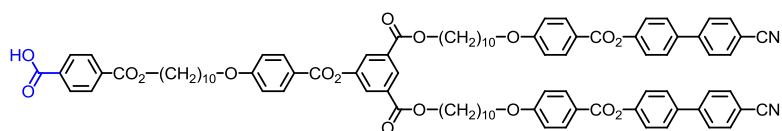


Figure 88 - Thermal-polarized optical micrograph of the nematic chiral texture displayed by compound **4** upon cooling the sample from the isotropic liquid to 128°C

Liquid-crystalline and thermal properties of compound 3: (investigated by POM and DSC) Laterally-branched mesogen **3** shows the formation of a chiral nematic (N^*) phase in accordance with the shape of the molecule which tends to orient parallel to one another in each plane, the latter being twisted from one another. (plane texture from the chiral nematic phase is shown in **Figure 88**). Phase transition temperature T (in °C) and phase transition enthalpy changes (ΔH in kJ/mol) of compound **3**: T_g 30 N^* 62 (nd) I.



Compound 4 – 1st generation cyanobiphenyl derivative bearing a carboxyl function

Name: Bis[10-(4-{{(4'-cyanobiphenyl-4-yl)oxy}carbonyl}phenoxy)decyl] 5-{4-[10-(4-carboxybenzoyloxy)decanoxy]benzoyloxy}benzene-1,3-dicarboxylate.

Synthesis of compound 4: To a solution of the aldehyde derivative^[4] (7.12 g; 4.75 mmol) into a mixture of THF (350 mL) and deionized water (70 mL), were added NaClO₂ (0.86 g; 9.51 mmol) and H₂NSO₃H (0.92 g; 9.51 mmol). The reaction mixture is stirred at room temperature during 2 hours. THF was evaporated under reduced pressure and the resulting aqueous solution was diluted into deionized water (500 mL). The product was extracted with CH₂Cl₂ and organic phases were gathered, dried over MgSO₄, and then evaporated to dryness under reduced pressure. The residue was dissolved in a minimum volume of CH₂Cl₂, and precipitation with methanol gave pure compound 2 as a white powder, yielding 86% (6.17g; 4.08 mmol).

NMR data of compound 4. ¹H-NMR (200 MHz, CDCl₃): 8,60 (t, 1H, H_{arom}); 8,19-8,12 (m, 10H, H_{arom}); 8,07 (d, 2H, H_{arom}); 7,77 et 7,69 (2d, system AB, 8H, H_{arom}); 7,64 (d, 4H, H_{arom}); 7,32 (d, 4H, H_{arom}); 6,98 (d, 6H, H_{arom}); 4,36 (t, 6H, CH₂O₂C); 4,04 (t, 6H, CH₂O); 1,86-1,75 (m, 12H, CH₂CH₂O et CH₂CH₂O₂C); 1,59-1,35 (m, 36H, aliphatic chains).

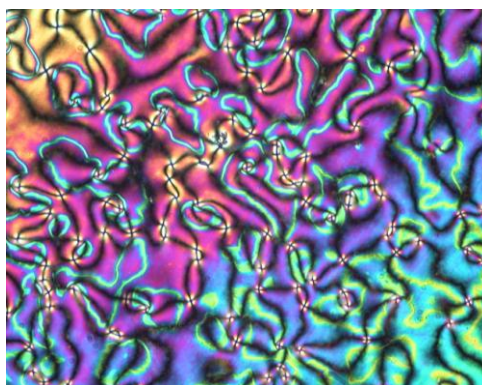
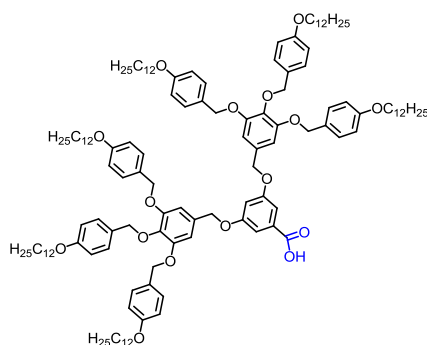


Figure 89 - Thermal-polarized optical micrograph of the texture displayed by **2** in the nematic phase upon cooling the sample from the isotropic liquid to 181°C

The liquid-crystalline phases could be identified by POM from their characteristic textures (nematic phase: schlieren texture; chiral nematic phase: plane texture)

Liquid-crystalline and thermal properties of compound 4: (investigated by POM and DSC) First generation cyanobiphenyl dendrimer **4** gives rise to a nematic phase. (schlieren texture from the nematic phase is shown in **Figure 89**). Phase transition temperature T (in °C) and phase transition enthalpy changes (ΔH in kJ/mol) of compound **4**: T_g 39 N. 194 (nd) I.



Compound 5 – 2nd generation polybenzylether dendron bearing a carboxylic acid function.

C₁₂H₂₅–SH ligand

¹H-NMR (400 MHz, CDCl₃) δ 2.52 (dd, $J = 7.5, 14.7$, 2H), 1.66 – 1.56 (m, 2H), 1.33 (t, $J = 7.7$, 2H), 1.26 (s, 15H), 0.88 (t, $J = 6.9$, 3H);

mud3eg ligand

¹H NMR (400 MHz, CD₃OD) δ 3.72 – 3.62 (m, 8H), 3.62 – 3.54 (m, 4H), 3.49 (t, $J = 6.5$, 2H), 2.51 (t, $J = 7.0$, 2H), 1.72 – 1.51 (m, 4H), 1.34 (s, 14H).

Particles characteristics synthesized in this work

Au/C₁₂H₂₅–SH

This particle synthesis was given as a detailed example in chapter 2.3.1.1.

¹H NMR (400 MHz, CD₃OD) δ 3.67 (m, 8H), 3.58 (m, 4H), 3.49 (t, $J = 6.5$, 2H), 2.51 (t, $J = 7.0$, 2H), 1.61 (m, 4H), 1.34 (s, 14H).

Au/G₁CB–SH

Particles **A**: ^1H -NMR (400 MHz, CD_2Cl_2): 8.46 (br. s, 1 arom. H); 8.12 (br. s, 4 arom. H); 7.87 (br. s, 2 arom. H); 7.66 (br. s, 12 arom. H); 7.30 (br. s, 4 arom. H); 6.95 (br. s, 4 arom. H); 4.28 (br. s, 4H, CO_2CH_2); 3.99 (br. s, 4H, CH_2O); 2.55 (br. s, 2H, CH_2CO_2); 1.74 (br. s, 10 aliph. H); 1.30 (br. s, 38 aliph. H).

Au/C₁₂H₂₅–SH±mud3eg

^1H NMR (400 MHz, CDCl_3) δ 3.67 (t, $J = 24.3$, 11H), 3.45 (s, 2H), 1.58 (s, 11H), 1.26 (s, 15H), 0.88 (s, 0.85H).

Au/C₁₂H₂₅–SH±G₁CB–SH

Particles **B**: ^1H -NMR (400 MHz, CD_2Cl_2 ; integration with respect to the signals of G₁CB–SH): 8.46 (br. s, 1 arom. H); 8.10 (br. s, 4 arom. H); 7.87 (br. s, 2 arom. H); 7.70 and 7.63 (2 br. s, 12 arom. H); 7.29 (br. s, 4 arom. H); 6.96 (br. s, 4 arom. H); 4.28 (br. s, 4H, CO_2CH_2); 4.00 (br. s, 4H, CH_2O); 2.55 (br. s, 2H, CH_2CO_2); 1.75 (br. s, 10 aliph. H); 1.65–0.97 (72 aliph. H); 0.85 (br. s, 5 aliph. H).

Au/pMP

The synthesis was carried out from derived Brust *et al.* one-phase method.^[5] Briefly, in the presence of acetic acid (3 mL), a 150 mL methanolic solution containing $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (300 mg, $7.6 \cdot 10^{-4}$ mol) into a 250 mL round bottom flask was vigorously stirred over a glass bath and a 50 mL solution of 4-mercaptophenol (230 mg, $1.82 \cdot 10^{-3}$ mol) was rapidly added and stirred during a short period of 10 to 15 minutes. Then a solution of NaBH_4 (445 mg, $1.18 \cdot 10^{-2}$ mol) prepared in 10 mL of mQ water at about 0°C was added dropwise into the flask. The reaction was kept under air and stirred during one hour. The water/methanol solution was then removed under reduced pressure and redissolved in 200 mL THF before it was diluted with 400 mL dichloromethane. This latter solution was washed 5 times with 250 mL deionized water and then the organic phases were evaporated before being suspended in a mixture of n-hexane/dichloromethane and centrifuged once 40 min at $14,240 \times g$ and 5 times 20 min at the same centrifugal force in dichloromethane only (or until TLC did not show any more trace of 4-mercaptophenol in supernatant). Dark residues were collected as a methanolic solution, filtered over a regenerated-cellulose 0.2- μm membrane and methanol was evaporated to give rise to a shiny black powder.

^1H NMR (400 MHz, CD_3OD) δ 7.92 – 7.08 (m, 2H), 7.02 – 6.06 (m, 2H).

Procedure for particle esterification: A solution of 25 mL of 4-mercaptophenol stabilized gold nanoparticles is prepared (50 mg, $1 \cdot 10^{-6}$ mol) and DCC is added (mg, mol) as well as DPTS (mg, mol) before compound $G_0^*-\text{COOH}$ or $G_1\text{CB}-\text{COOH}$ was added in a 5-mL dichloromethane solution to the flask (50 mg, $5.7 \cdot 10^{-5}$ mol or 95 mg, $6.2 \cdot 10^{-5}$ mol respectively). The reaction was kept under a slow stirring and under argon for 72 hours. The solution was washed many times with deionized water before the dichloromethane solution was evaporated under reduced pressure and their contents transferred to a THF solution to be purified by Bio-Rad Bio-Beads S-X1 size exclusion chromatography (1% cross-linked; separated molecular weights: 600 – 14000 Da). The selected fractions according to UV-Vis spectra gave rise to particles **C** or **D** with compound **1** or **2** esterified respectively.

Au/pMP} $G_0^*-\text{COOH}$

Particles **C** (including a mixed coverage of $G_0^*-\text{COOH}$ and 4-mercaptophenol on gold particles): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.56 impurity, 8.34-7.76 (3 br. s, 7H), 7.75-7.43 (2 br. s, 6H), 7.42-7.04 (3 br. s, 6H), 7.03-6.83 (br. s, 2H), 6.78-6.40 (2 br. s, 2H), 6.06 impurity, 4.31 (br. s, 2H), 4.15-3.73 (3 br. S, 6H), 1.96-1.68 (2 br. s, 7H), 1.66-1.22 (3 br. s, 16H), 1.13 – 0.79 (m, 9H).

Au/pMP} $G_1\text{CB}-\text{COOH}$

Particles **D** (including a mixed coverage of $G_1\text{CB}-\text{COOH}$ and 4-mercaptophenol on gold particles): ^1H NMR (400 MHz, CD_2Cl_2) δ 8.50 (br. s, 1H), 8.02 (3 br. S, 10H), 7.67 (2 br. s, 12H), 7.39 – 7.12 (m, 6H), 7.05 – 6.79 (m, 8H), 6.58 (s, 1H), 4.30 (s, 5H), 3.99 (s, 6H), 1.76 (s, 14H), 1.43 (s, 42H), 0.08 (s, 6H).

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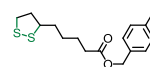
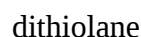
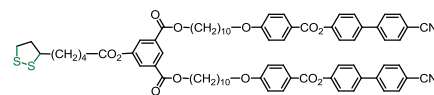
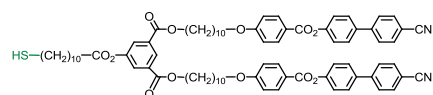
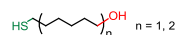
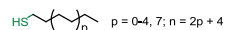
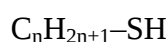
Third appendix

A schematic representation of nanoparticles and ligands used to synthesize the latter is given in the following lines

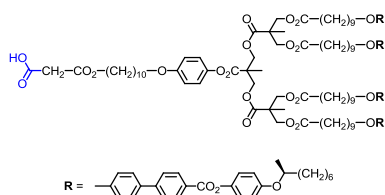
Formalism

Gold nanoparticles (AuNPs) are synthesized according to a modified Brust's protocol. They are stabilized by alkanethiols ($R-SH$, i.e. $C_nH_{2n+1}-SH$). They will be noted as $Au/C_nH_{2n+1}-SH$. If a second ligand (e.g. *m*-mercaptoalkan-1-ol, $HS-C_mH_{2m+1}-OH$) is present, the mixed monolayer on AuNPs is noted: $C_nH_{2n+1}-SH|HS-C_mH_{2m+1}-OH$. When the proportions are determined, AuNPs (e.g. containing 269 gold atoms on average) are noted as follows: $Au_{269}/C_nH_{2n+1}-SH_{0.6}|HS-C_mH_{2m+1}-OH_{0.4}$ for 60 % of alkanethiol and 40 % of hydroxyalkanethiol in the stabilizing shell. Moreover, mixed monolayers can result from a ligand exchange reaction, in that case, the AuNPs are noted: $Au_{269}/C_nH_{2n+1}-SH_{0.6}\pm HS-C_mH_{2m+1}-OH_{0.4}$, the first ligand named being the original stabilizing one, the second being the exchanged one, and the respective ratios are subscripted. Finally dendrimers bearing a carboxylic function can be esterified on such AuNPs, in the case of esterification of first-generation cyanobiphenyl bearing a carboxylic acid, the resulting AuNPs are noted: $Au_{269}/C_nH_{2n+1}-SH_{0.6}\pm HS-C_mH_{2m+1}-OH_{0.4}\}G_1CB-COOH_{0.3}$ when 30 % of dendrons are estimated to lie in the shell after purification.

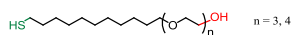
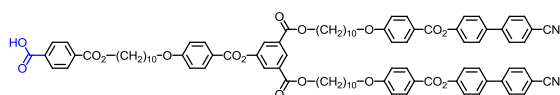
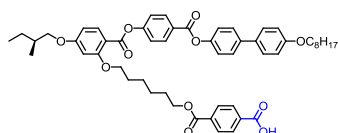
Ligands for AuNPs



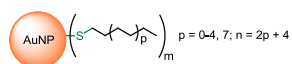
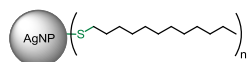
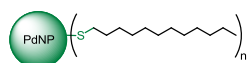
HY43



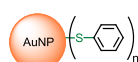
mud3eg, mud4eg

G₁CB-COOHG₀*-COOH

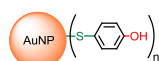
NPs – direct synthesis

Au/C_nH_{2n+1}-SH; n = 4-12, 18Ag/C₁₂H₂₅-SHPd/C₁₂H₂₅-SH

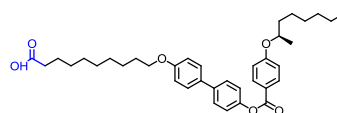
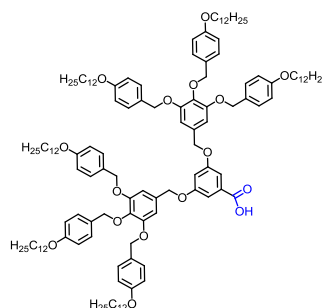
Au/BT



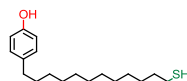
Au/pMP



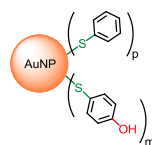
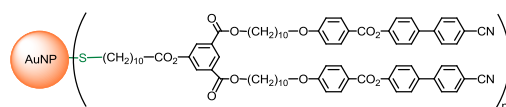
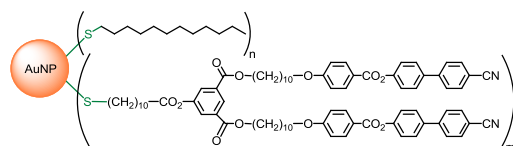
CK35

G₂-Percec-COOH

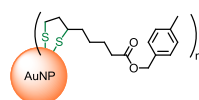
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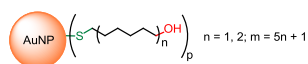
Au/BT|pMP

Au/G₁CB-SHAu/C₁₂H₂₅-SH|G₁CB-SH

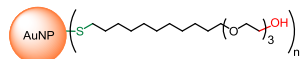
Au/dithiolane



Au/HS-C_mH_{2m}-OH; m = 6, 11



Au/mud3eg

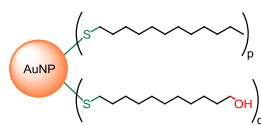


Au/PPh₃

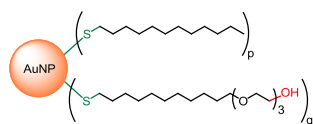


NPs – ligand exchange

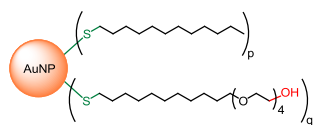
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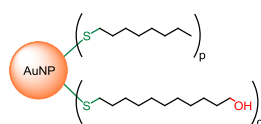
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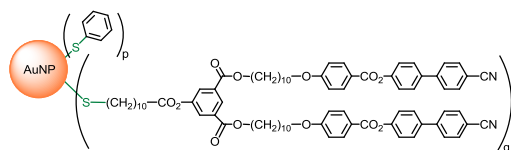
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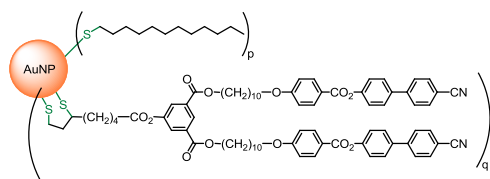
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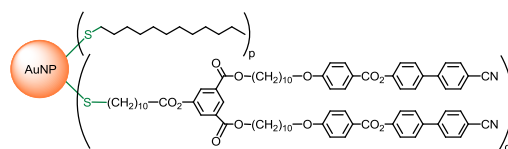
Au/BT±G₁CB-SH



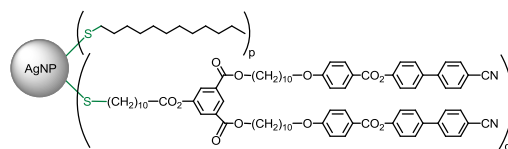
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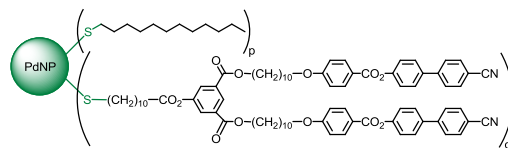
Au/C₁₂H₂₅-SH±G₁CB-SH



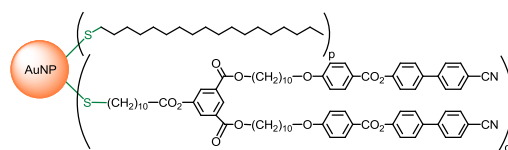
Ag/C₁₂H₂₅-SH±G₁CB-SH



Pd/C₁₂H₂₅-SH±G₁CB-SH

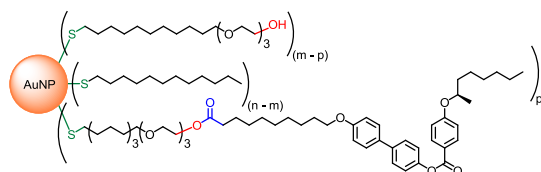


Au/C₁₈H₃₇-SH±G₁CB-SH

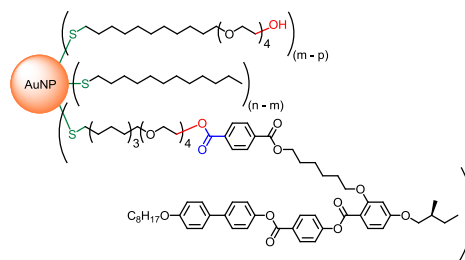


AuNPs – esterification

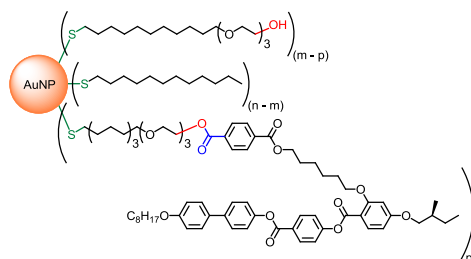
Au/C₁₂H₂₅-SH±mud3eg}CK35



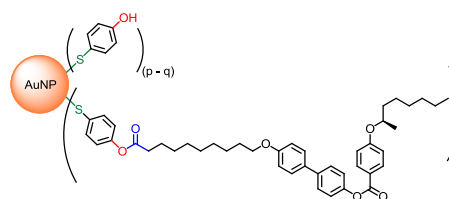
Au/C₁₂H₂₅-SH±mud4eg}G₀*-COOH



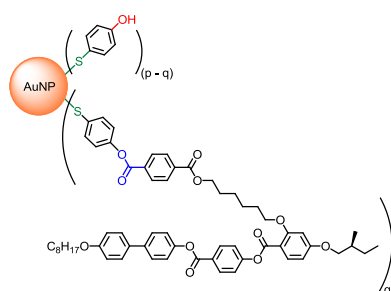
Au/C₁₂H₂₅-SH±mud3eg}G₀*-COOH



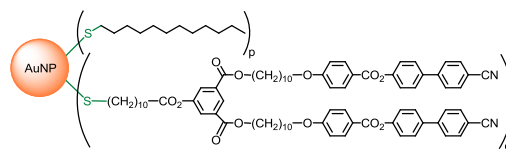
Au/pMP}CK35



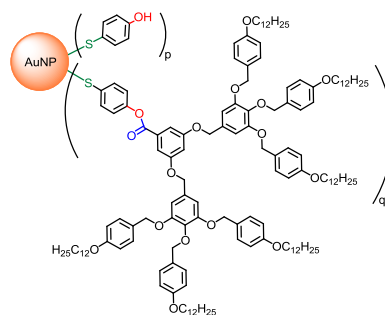
Au/pMP}G₀*-COOH



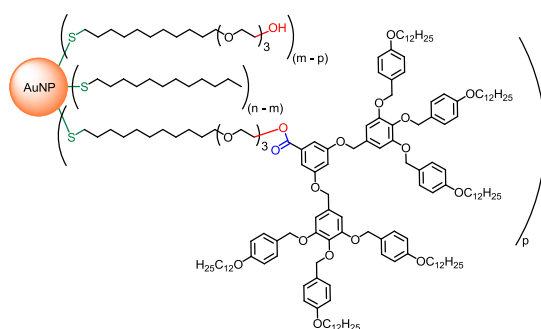
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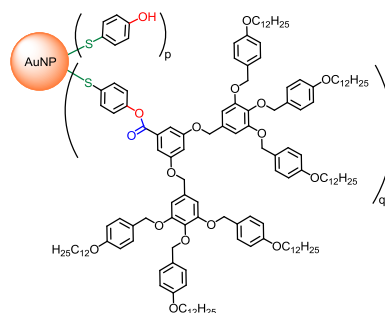
Au/pMP}G2-Percec

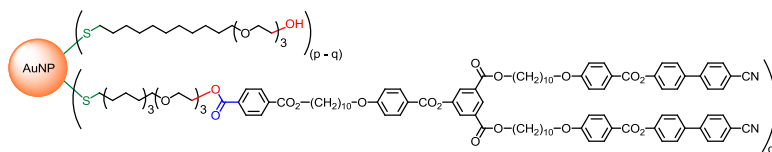
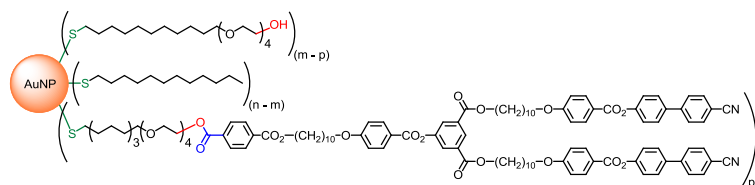
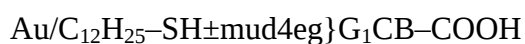
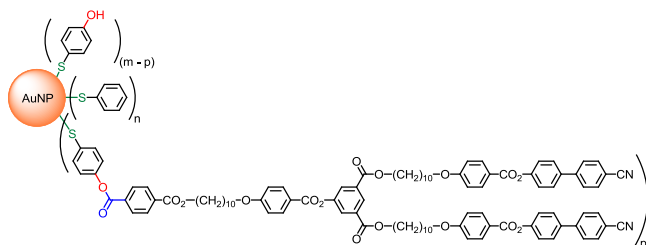
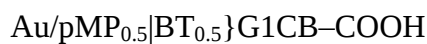
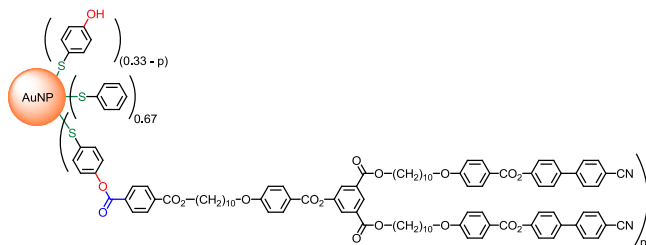
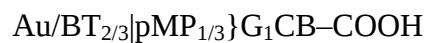
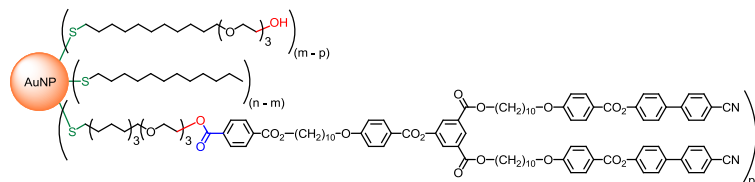
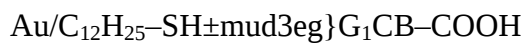
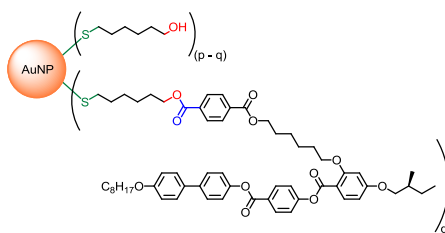


Au/C₁₂H₂₅-SH±mud3eg}G₂-Percec-COOH



Au/pMP}HY83





Fourth appendix

These calculations follow the work of Murray *et al.*^[6]

Cluster Dimensions and Molecular Weight, Model of the Cluster Core.

The following enlarges on a dimensional model of the cluster molecules and their cores.

From the present data, estimates of the molecular weight and thiolate surface coverage of the cluster require structural models of the gold core *shape*. Such models reflect the numbers of gold atoms on the surface and in the entire particle, for comparison to elemental analysis results. Two shapes are modeled, a sphere and a cuboctahedron.

The spherical model takes the gold core as a sphere with density ρ_{Au} (assuming that of bulk gold) covered with a “skin” of hexagonally close-packed gold atoms. We label this a “continuum” model. The radius of the “skin” is taken as the center of the atoms on the skin (at $R_{Core} - R_{Au}$), to avoid overestimating the number of surface atoms. The relation is

$$\chi_{organic} = \frac{4\pi(R_{Core}-R_{Au})^2(\rho_{HCP})(MW_{Thiol})\gamma}{4\pi(R_{Core}-R_{Au})^2(\rho_{HCP})(MW_{Thiol})\gamma + \frac{4}{3}\pi R_{Core}^3(\rho_{Au})(AW_{Au})} \quad (\text{Equation 1})$$

where $\chi_{organic}$ is the mass fraction of alkanethiolate in the cluster, R_{Au} the crystallographic radius of a gold atom (0.145 nm), ρ_{HCP} the number density of surface gold atoms (13.89 atoms/nm², assuming hexagonal close packing), MW_{Thiol} the alkanethiol molecular weight in mass/molecule, γ the coverage (ratio of alkanethiolates to surface Au atoms), ρ_{Au} the atom density of bulk gold (58.01 atoms/nm³), and AW_{Au} the Au atomic weight in mass/atom. The numerator in Equation 1 and the first term in the denominator represent the alkanethiolate mass on the surface of the Au core. The second term in the denominator represents the Au core mass. Since $\chi_{organic}$ depends on the model’s prediction of the surface: volume ratio of gold atoms, as checked with a simple

computer program. Assuming a “spherical” core, the program counts the number of surface and total atoms contained within spheres of various radii superimposed on an FCC lattice. The FCC and “continuum” predictions of surface:volume atom ratios were in good agreement in the expected sphere size range.

The C_{12} surface coverage of alkanethiolates was determined as $\gamma = 0.66$ by solving the Equation 1 taking the R_{Core} value determined by SAXS (11.9 Å) and $\chi_{organic}$ the elemental and TGA analyses. The spherical model, for this R_{Core} value, predicts that the core will contain 409 Au atoms, of which 191 lie on its surface. Thus, if this model is accurate, there are 126 alkanethiolate chains or 2 for every 3 surface gold atoms. This coverage is *twice* that seen for monolayers on planar hexagonally close-packed Au(111) surfaces ($\gamma = 0.33$), requiring Au–S sites to be more densely packed on the surface of the Au cluster compound. This may reflect the small R_{Core} value which splays the attached alkanethiol chains outward from one another, relieving steric crowding, and/or the reactivity of atoms on the highly curved core surface (relative to planar gold). Turning to the other core model, high-resolution TEM of the C_{12} cluster suggested cuboctahedral-shaped cores, so we consider a cuboctahedron for the C_{12} clusters. A perfect cuboctahedral gold cluster closest to a 12 Å, “radius” consists of either 309 or 561 total atoms (so-called “magic numbers”), and has 162 or 252 surface atoms, respectively. Modeling the clusters as Au_{309} and Au_{561} cuboctahedra returns γ values of 0.59 and 0.69, respectively, which are not very different from those predicted for “spherical” cores. This is because cuboctahedra have nearly the same ratio of surface atoms to total atoms as do the fictitious spheres of the “continuum” model, Equation 1. Taking the cuboctahedron structure into account adds to this picture, moreover. A Au_{309} cluster would have 60 “edge” surface atoms, and 102 on flat faces, an arrangement leaving precisely one alkanethiolate per 3 gold atoms on the flat faces (in agreement with the $\gamma = 0.33$ observed for alkanethiolate monolayers on hexagonally close-packed planar gold) if all “edge” atoms are assumed to bind one (sterically relatively unencumbered) alkanethiolate.

We do not have in hand SAXS determinations of the core radii of the C_8 and C_{16} clusters, but returning to the spherical model, the “continuum” model Equation 1 can be solved for R_{Core} assuming the coverage result from the C_{12} cluster ($\gamma = 0.66$). This gives $R_{Core} =$

10.7 Å, (C₈ clusters) and 8.5 Å, (C₁₆ clusters, Table 3). Considering the approximations, there clearly is not a *large* change in the average core size with alkanethiol chain length. Further SAXS measurements will resolve these features.

Last, analysis of the SAXS intensities in the C₁₂ cluster R_{Core} measurement suggests a Au core population close to that of the cuboctahedral model. Equation 1 with $R_{Core} = 11.9$ Å, (the SAXS result) and $\gamma = 0.66$ predicts an average C₁₂ cluster “molecular weight” of 106 000 g/mol, in the mass range of many biomolecules. The 309 and 561 atom cuboctahedra MW would be 80 000 and 140 000 g/mol, respectively. Mass spectral molecular weight measurements should help to resolve the shape issue.

Small Angle X-ray Scattering (SAXS): Metal clusters with hydrocarbon ligands and in hydrocarbon solvents are ideal SAXS substrates because the X-ray scattering is dominated by the metal core and contributions from the ligand shell and solvent are minimal. SAXS data should exhibit large signal-to-noise ratios and intensities (I) scaling linearly with concentration (i.e., cluster-cluster scattering is unimportant). The cluster core sizes can be then deduced from the SAXS data based on two approaches.

The first approach is Guinier plots ($\ln(I(q))$ vs. q^2 is linear) taken over small and large scattering angles serve to estimate the largest and smallest core sizes (radius of gyration, $R_{G,max}$ and $R_{G,min}$), respectively, present in sufficient quantities to appreciably contribute to the scattered intensity. At small scattering angles ($q = 4\pi (\sin \theta) / \lambda$, where λ is wavelength and 2θ the angle of scattering, thus q is typically in units of Å⁻¹), the largest clusters dominate the scattering, whereas at higher scattering angles, the smaller particles dominate.

The second SAXS data analysis uses Porod plots ($q^4 I(q)$ vs. q), the maxima of which can give reliable estimates ($0.9 / q_{min} = 0.54 / q_{max} = \text{diameter in nm}$)^[7] of core size because the Au/ligand interface has a sharp transition in electron density. The Porod plots reasonably estimate the radius R_{POROD} of the smallest particles that have a significant population in the size dispersion.

Murray noticed that both R_{POROD} and $R_{G,min}$ nicely compare to R_{TEM} . In contrast, the SAXS $R_{G,max}$ are considerably larger, reflecting the fact that the TEM values are averages from histograms; that is, numerically, the larger radii clusters constitute a minority population in the preparations.^[6, 8]

Elemental analysis: Compositional analysis for C, H, S, and Au can be performed giving percentage weights that allow the determination of the organic/inorganic ratio. It appeared that % (C + H + S) are in relatively good agreement with TGA analysis but it was also found that the Au content is generally under-reported.^[6]

List of publications

Publications related to the subject

- ✦ Liquid-crystalline moieties onto gold nanoparticles, J. Boudon, S. Frein, T. Scharf, G. Süss-Fink, T. Bürgi and R. Deschenaux, manuscript in preparation
- ✦ Liquid-Crystalline Thiol- and Disulfide-Based Dendrimers for the Functionalization of Gold Nanoparticles, S. Frein, J. Boudon, M. Vonlanthen, T. Scharf, J. Barberá, G. Süss-Fink, T. Bürgi and R. Deschenaux, *Helv. Chim. Acta* **2008**, 91 (12), 2321-2337, doi: 10.1002/hlca.200890253

Publications stemming from collaborations

- ✦ Ligand Exchange on Au₂₅ Cluster with Chiral Thiols, S. Si, C. Gautier, J. Boudon and T. Bürgi, *J. Phys. Chem. C* **2009**, 113 (30), 12966-12969, doi: 10.1021/jp9044385
- ✦ Shape- and Size-Selective Preparation of Hectorite-Supported Ruthenium Nanoparticles for the Catalytic Hydrogenation of Benzene, G. Süss-Fink, F.-A. Khan, J. Boudon and V. Spassov, *J. Clust. Sci.* **2009**, 20 (2), 341-353 doi: 10.1007/s10876-009-0246-5
- ✦ Adsorption of Thiol-Protected Gold Nanoparticles on TiO₂ and Their Behavior under UV Light Irradiation, I. Dolamic, C. Gautier, J. Boudon, N. Shalkevich and T. Bürgi, *J. Phys. Chem. C* **2008**, 112 (15), 5816-5824, doi: 10.1021/jp711442m
- ✦ Probing Chiral nanoparticles and surfaces by infrared Spectroscopy, C. Gautier, M. Bieri, I. Dolamic, S. Angeloni, J. Boudon and T. Bürgi, *Chimia* **2006**, 60 (11), 777-782, doi: 10.2533/chimia.2006.777

Publications from previous work

- ✦ The First Catalytic Method For Heck Alkynylation Of Unactivated Aryl Bromides (Copper-Free Sonogashira) in an Ionic Liquid: 1 mol-% Palladium/Triphenylphosphane/Pyrrolidine In [BMIM][BF₄] as a Simple, Inexpensive and Recyclable System, J.-C. Hierso, J. Boudon, M. Picquet, and P. Meunier, *Eur. J. Org. Chem.* **2007**, (4), 583-587, doi: 10.1002/ejoc.20060976
- ✦ {1,1'-Bis[bis(5-methyl-2-furyl)phosphino]ferrocene- κ^2P,P' } dichloroplatinum (II) dichloromethane hemisolvate, A. Fihri, J. Boudon, J.-C. Hierso, R. Amardeil, P. Meunier and P. Richard, *Acta Crystallogr.* **2005**, E61 (11), m2267-m2269, doi: 10.1107/S1600536805032034

Curriculum Vitae

Julien Boudon, born in March, 1979, in France

Education

- 2002 **Bachelor of science** in Material Science, Université de Bourgogne in Dijon,
- 2004 **Master of Science & Technology** in Analytical Chemistry, Université de Bourgogne in Dijon, France
- 2005 **Master of Science** in Molecular Chemistry and Green Processes, Université de Bourgogne in Dijon
- 2009 **PhD Thesis** within Prof. Thomas Bürgi's group in the laboratory of Physical Chemistry, Université de Neuchâtel, Switzerland

Internships

- 2004 Elaboration of proportioning method in HPLC for a new insecticide at Condat lubricants in Chasse sur Rhône, France
- 2005 Study of catalytic systems of palladium/(ferrocenic triphosphine) ligand for enyne cross-coupling in an ionic liquid – Université de Bourgogne, France

Communications

- 2006 **October**, PhD symposium at EMPA St. Gallen, Switzerland
Oral Presentation
- 2007 **August**, Summer school in Villars-sur-Ollon, Switzerland
Poster Presentation
September, Fall Meeting of the Swiss Chemical Society, at EPF Lausanne, Switzerland
Poster presentation
- 2008 **September**, Fall Meeting of the Swiss Chemical Society, at ETH Zürich, Switzerland
Poster presentation
September, 6th NanoEurope Congress in St. Gallen, Switzerland
Poster presentation, Award for the best poster
September, 1st BioForum in Neuchâtel, Switzerland
Poster presentation
September, 6th International Conference on Inorganic Materials in Dresden, Germany
Poster presentation

Communications (continuation)

- 2009 **March, 1st** International Conference on Multifunctional, Hybrid and Nanomaterials in Tours, France
 Poster presentation
- April, 10th** European Conference on Liquid Crystals in Colmar, France
 Poster presentation
- July, 5th** International Conference on Gold Science, Technology and Its Applications in Heidelberg, Germany
 Oral presentation
- September**, Fall Meeting of the Swiss Chemical Society, at EFP Lausanne, Switzerland
 Poster presentation