Organization of Gold Nanoparticles Covered by Liquid-Crystalline Dendrimers

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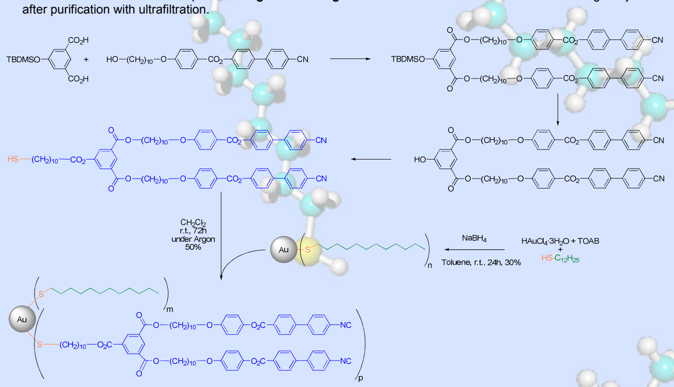
Introduction

Gold nanoparticles have generated a growing interest in the past two decades due to their interesting properties and potential applications. [1] Gold particles covered by liquid-crystalline dendrimers are a basis for the elaboration of new optical materials. [2] Such composite materials could organize in such a way that the gold cores self-assemble in evenly spaced rows due to mutual interactions between the dendrimer shells. Organized structures of this type may find applications in optical devices such as in optical waveguides or diffraction gratings due to large local variation of the refractive index. Particularly interesting is the fact that very short periodicities can be obtained by this strategy.

Synthesis

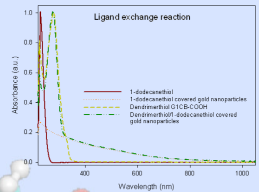
○ Liquid-crystalline dendrimer-covered gold nanoparticles :

First, a thiolated **1st-generation liquid-crystalline** (G1LC) **dendrimer** bearing cyanobiphenyl units was synthesized. Then to previously synthesized 1-dodecanethiol-covered gold nanoparticles was added a predefined amount of G1LC dendrimer to perform a **ligand exchange** reaction. The final material was obtained in good yield after purification with ultrafiltration.

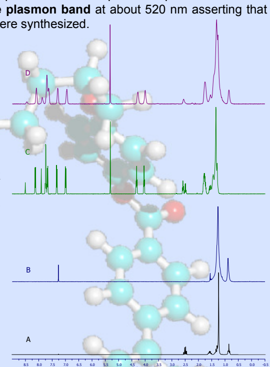


This method benefits from mainly two advantages: it leads to **full coverage** with the desired thiol derivative on the nanoparticles which **size can be controlled**; the **loading** of the desired thiol derivative **can be selected** so that the **ligands ratio can be adjusted**.

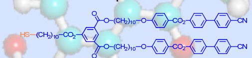
Characterization

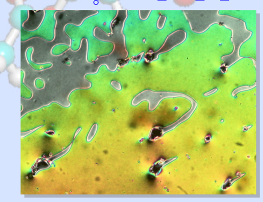


UV-visible spectroscopy was used to follow ligand exchange reaction evolution and purification. The spectra of particles show **no characteristic surface plasmon band** at about 520 nm asserting that **very small particles** were synthesized.



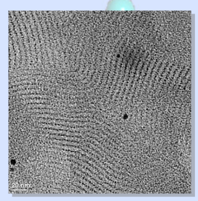
NMR spectroscopy was used to elucidate the structure and check the purity of the gold nanoparticles. Parts B and D: **broadening** for the thiol derivatives grafted on the gold (if compared to parts A and C of free ligands) and **disappearance** of CH_2SH signal are **proof of grafting** and **no sharp peaks** proof of **no free thiol** in the samples. Part D: *ca.* 40% of dendrimer-thiol on particles.





$Tg \xrightarrow{17°C} SmA \xrightarrow{162°C} N \xrightarrow{175°C} I$

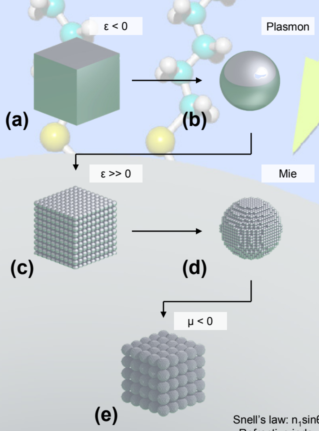
Polarized optical microscopy as well as differential scanning calorimetry (not shown) were used to investigate the liquid-crystalline and thermal properties of the thiolated dendrimer. This dendron gave rise to a **smectic A** phase and to a **nematic** phase (Left: nematic phase obtained upon cooling the sample from the isotropic liquid to 173°C).



Transmission electron microscopy was used to check the size and size distribution (**1.2 ± 0.4 nm**, sample of 1755 particles, min. size 0.74 nm, max. size 6.98 nm).

Applications and Outlook

The main idea consists in creating an artificial three-dimensional structure composed of 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 much smaller than the wavelength of light. 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 indexes. [5, 6]

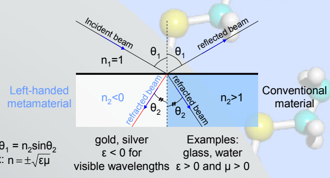


Using a noble metal such as gold provides a large negative real part of the permittivity ($\varepsilon < 0$; part **(a)**) and nanoparticles made of it support localized surface plasmons (LSP) for appropriate wavelengths (part **(b)**).

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 ($\varepsilon >> 0$; 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)**). [6]

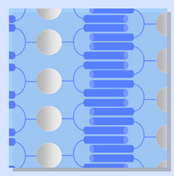


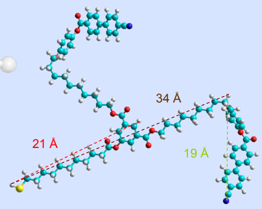
Snell's law: $n_1 \sin\theta_1 = n_2 \sin\theta_2$
Refractive index: $n = \pm\sqrt{\varepsilon\mu}$

Considerable advantages could be achieved with a **bottom-up technique** based on the **self-assembly of liquid-crystal coated** (gold) **nanoparticles** which could **operate in the visible** spectral domain. [6] In addition, here is a list of potential applications of such materials: superlens (an optical lens which exceeds the diffraction limit), cloaking devices (surrounding the object to be cloaked with a shell which affects the passage of light near it), light or electromagnetic trap, improved Bragg mirror, etc.

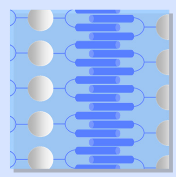
Organization

Thiolated dendrimers attached to gold nanoparticles promoted an unexpected **surface organization** on carbon-coated copper grids: the particles arrange in evenly spaced rows (TEM pictures above and below). The new material obtained showed a surface organization at the nanometer scale although no clear mesomorphic properties were observed at a macroscale level.

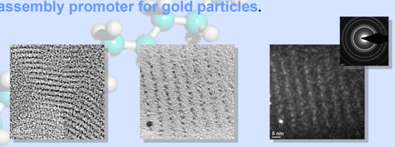




Schematic representations of interdigitation of the cyanobiphenyl mesogenic units from one layer to the adjacent one (dendrimer arms are represented as blue cylinders and grey spheres represent gold cores).



This can be interpreted as the **formation of layers**, as for smectic phases. Thus, the chosen thiolated dendrimer acts as a **self-assembly promoter for gold particles**.



Conclusion

These materials were obtained by ligand exchange, with gold nanoparticles synthesized prior to this. *i.e.* the stabilizing-alkylthiol ligands were exchanged for the appropriate liquid-crystalline dendrimer-thiols. [2] This method represents a convenient way to prepare gold nanoparticles with different ratios of dendrimers to alkylthiol ligands attached to their surface. Contrary to recent studies [3,4] our first materials based on lower generation dendrons did not show a clear mesomorphic behaviour in the bulk. On the other hand a surface organization on the nanometer scale was observed when spreading the materials onto a carbon-coated copper grid, opening the way to further design of organometallic materials with temperature-dependent optical properties with a bottom-up approach.

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