Gold Nanoparticles Functionalized with Liquid-Crystalline Dendrimer-Thiols

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Surface Spectroscopy & Nanosciences

○ Motivations

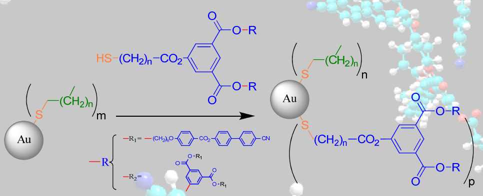
Gold nanoparticles have generated a growing interest in the past two decades due to their metallic properties and potential applications.[1] We proposed gold particles stabilized by liquid-crystalline thiolated dendrimers in order to obtain materials with temperature-dependent optical properties as it was observed with mesomorphic fullerene- and ferrocene-containing dendrimers.[2]

○ Objective

As the first attempts with lower generation dendrons did not show a clear mesomorphic behaviour, higher-generation dendrimers of this type will be studied in next experiments and thus thermal behaviour of these new materials will be discussed with a view to using them as optical materials provided a three-dimensional arrangement.

○ Principle

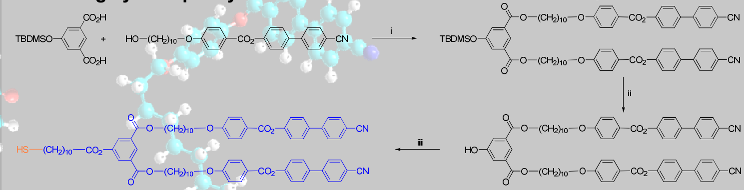
These materials were obtained by exchanging stabilizing-alkylthiol ligands for the appropriate liquid-crystalline dendrimer-thiol on gold nanoparticles.



The final material with a mixed coverage was obtained *via* the control of the ligand ratio through the ligand exchange reaction.

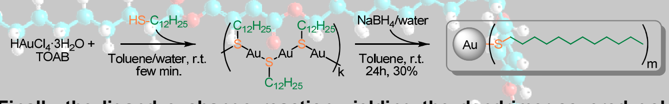
○ Design methodology

Here we report the synthesis of the first generation thiolated dendrimer bearing cyanobiphenyl units:

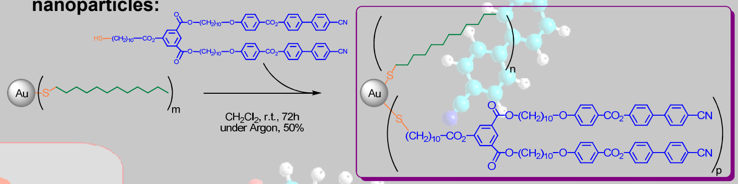


i) CH_2Cl_2, DCC, DPTS, 4-ppy, r.t. 40 h, 94%. ii) THF, $Zn(BF_4)_2$. 6-7 H_2O, 50°C 24 h, quant. iii) 11-Mercaptoundecanoic acid, 4-(dimethylamino)pyridinium toluene-para-sulfonate (DPTS), *N,N'*-dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine (4-ppy), CH_2Cl_2, r.t., 24 h; 46%

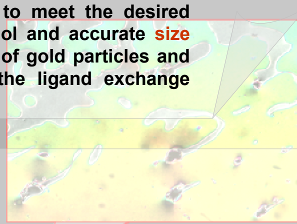
As well as 1-dodecanethiol stabilized gold nanoparticles as a starting material for ligand exchange reaction:



Finally the ligand exchange reaction yielding the dendrimer-covered gold nanoparticles:

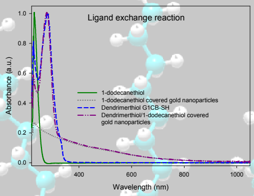


In this strategy, dendrimer can be tailored to meet the desired properties. a full coverage with alkylated thiol and accurate size control can be reached during the synthesis of gold particles and the ligand ratio can be adjusted through the ligand exchange reaction.

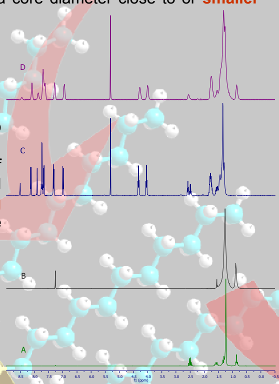


○ Results

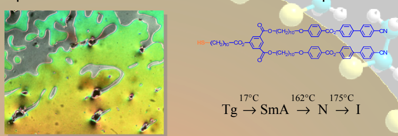
Our material was characterized with different spectroscopic techniques leading to crucial information such as size of particles, their size distribution and the purity needed for potential applications.



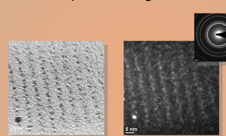
UV-visible is the chosen technique to follow the ligand exchange reaction evolution and purification. There is no characteristic plasmon band at about 520 nm which is proof of particles with a core diameter close to or smaller than 2 nm.



NMR spectroscopy was used to determine the ligand ratio as well as the purity of the material. 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 a proof of grafting and no sharp peaks a proof of no free thiol in the samples. Part D: *ca.* 40% of dendrimer-thiol on particles.



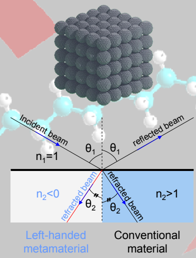
Polarized optical microscopy as well as differential scanning calorimetry (not shown) were used to investigate the liquid-crystalline and thermal properties of the thiolated dendrimer. This dendron gave rise to smectic A and nematic phases (Above: nematic phase obtained at 173°C upon cooling from the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



Transmission electron microscopy confirmed UV-visible predictions concerning the size (1.2 ± 0.4 nm). It even showed a surface organization of particles in evenly spaced rows on carbon coated copper grids interpreted as the formation of layers as for smectic phases.

○ Applications

As reported recently in the literature,[3] such a material composed of unit cells (nanoparticles) surrounded by an organizing media (liquid-crystalline dendrimer coating) can reach unique optical properties provided that it self-organizes in well-ordered and controlled arrays much smaller than the wavelength of light.



Conceptual sketch of the artificial three-dimensional material organized in such a way that one could access negative refractive indices (the so-called metamaterials).

In such a material the light is refracted on the same side of the normal on entering the material (Snell's law for $n_2<0$: $n_1 \sin\theta_1 = n_2 \sin\theta_2$).

Considerable advantages could be achieved with a bottom-up approach based on the self-organization of liquid crystal coated gold nanoparticles which could operate in the visible part of the electromagnetic spectrum.

Let us imagine the way to make an object appear invisible by bending the light around it so that the waves seem to pass through empty space!

○ Outlook

- **superlens (an optical lens which exceed the diffraction limit);**
- **cloacking device (surrounding the object to be cloacked with a shell that affects the passage of light near it);**
- **light or electromagnetic trap;**
- **improved Bragg mirror.**

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