When dendrimer-functionalized gold nanoparticles lead to dramatic two-dimensional arrangement

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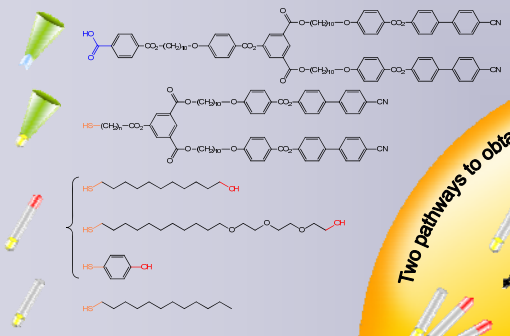
Background

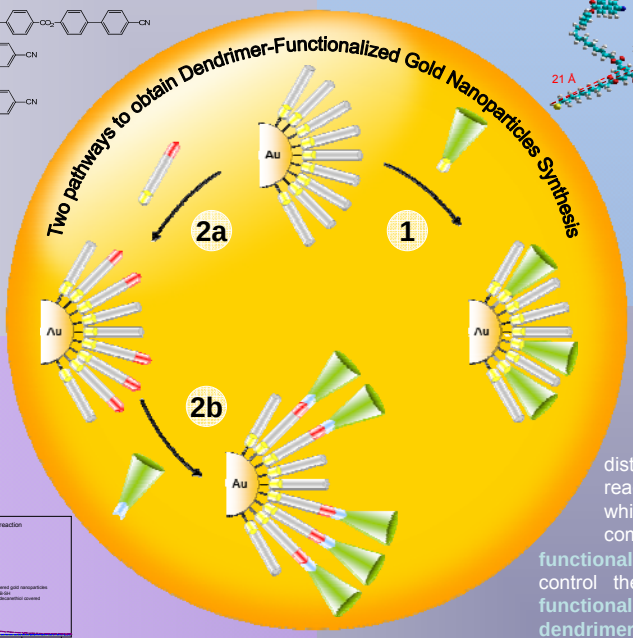
Recent studies have demonstrated the possibility to functionalize gold nanoparticles[1] (AuNPs) that are currently fashionable materials with liquid-crystalline (LC) dendrimers by exchanging stabilizing thiol-ligands with dendrimer thiols.[2,3] We have developed a three-step method avoiding the limiting dendrimer-thiol step in order to prepare tailored dendrimer-functionalized AuNPs. This new material shows an amazing two-dimensional arrangement.

Introduction

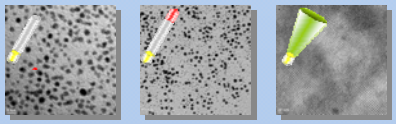
Previous procedures[4,5] were adapted to obtain well-defined monolayer protected particles derivatized from the original Brust *et al.* method.[4,6] Then ligand exchange reaction[7,8] was performed to introduce the desired functional groups. Finally, new molecular building blocks were obtained by tethering dendrimers to the chemically functionalized AuNPs.[5]

Legend



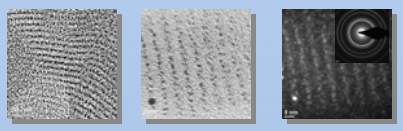


Organization



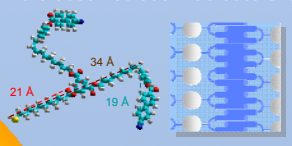
On the left, initial AuNPs stabilized by alkanethiols only. **In the middle**, AuNPs a mixed shell of alkanethiols and ω-hydroxyalkanethiols. **On the right**: dendrimerthiol functionalized AuNPs (scale bar 20 nm).

AuNPs coated with or without functional groups on **alkanethiol ligands** did **not show any organization** and only particles containing dendrimers in their shell displayed a surface organization. This demonstrates the ability of the **dendrimer** used to **promote a self-organization** on TEM carbon coated copper grids.



Left & middle: bright field TEM micrographs showing rows of thiolated dendrimer-coated AuNPs (20 and 5 nm scales resp.). **Right**: dark field and electron diffraction pattern of the corresponding area of the image in the middle.

The particles arrange in **evenly spaced rows** and the new material obtained showed a **surface organization** at the nanometer scale although no clear mesomorphic properties were observed at a macroscale level.

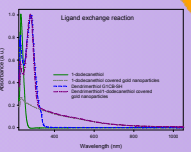


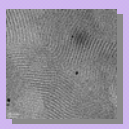
Left: Scheme of thiolated dendrimer showing lengths. **Right**: proposed interdigitation of dendrimer arms (blue) and organization of gold cores (grey).

Particle cores within one row are closely packed, and separated from each other by 1.3 times the length of a dendrimer unit. This can be interpreted as the formation of layers, as for smectic phases, with **interdigitation of the cyanobipenyl mesogenic units** from one layer to the adjacent one.

Characterization

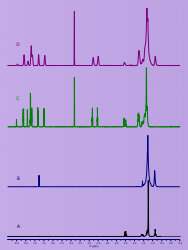
UV-visible spectroscopy was used to follow ligand exchange reaction **evolution** and **purification**. The spectra of particles show no characteristic surface plasmon band at about 520 nm asserting that very **small particles** were synthesized.





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).

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.



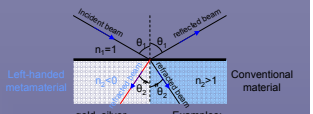
Polarized optical microscopy and differential scanning calorimetry (not shown) were used to investigate the liquid-crystalline and thermal properties of the **thiolated dendrimer**. This dendron gave rise to **smectic A** and **nematic** phases.
(**Here**: nematic phase obtained at 173°C upon cooling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

Method

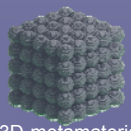
In our project, alkanethiols are a convenient way to stabilize AuNPs while controlling accurately particle size and size distribution. On the other hand, ligand exchange reaction allows one to introduce functional groups while keeping the particle size. Both techniques combined are a good way to **limit the number of functional groups** on the AuNPs surface and precisely control their size in the mean time. With **alcohol functional groups** it becomes an easy task to **esterify dendrimers bearing a carboxylic acid group**. In this manner, various hydroxyl-functionalized thiol ligands and acid-dendrimers can be combined. Our latest investigations have shown that **once first-generation LC cyanobiphenyl-dendrimers are attached, 2D organization of particles is observed on a surface** (see TEM pictures): AuNPs are aligned in rows, which are separated by a little more than the distance of a fully stretched dendrimer.

Applications

Cloaking device



Negative Refraction



3D-metamaterial

Conclusion & Outlook

Dendrimer-functionalized AuNPs are fascinating hybrid materials that combine the features of dendrimers and the properties of metal nanoparticles and give rise to versatile building blocks in nanofabrication.[9] Mesomorphic properties of such LC AuNPs could lead to materials with temperature-dependant optical properties and more.[10]

Acknowledgement

The Swiss National Science Foundation is greatly acknowledged for financial support
CSEM SA is acknowledged for TEM facilities

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International Conference on Inorganic Materials – Dresden, Germany
28-30th September 2008

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