

SUB-NANOMETER AU MPCs SYNTHESIZED BY MULTIPODAND CALIXARENE PROTECTION

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Monolayer-protected Au clusters^[1] (MPCs) have aroused significant scientific interest because these structures are known to be useful in many fields such as optoelectronics, catalysis and molecular sensing.^[2] MPCs of subnanometer core dimension are particularly enticing owing to their quantum size effects.^[3] Indeed, it is known that as the core size decreases under the nanometer limit, the particles attain discrete electronic states and thus can show semiconductor-like electronic properties. The preparation of these compounds through direct methods has been, however, restricted to nanoparticles in which the gold passivation has been obtained with specific ligands such as tripeptides (glutathione), mercaptosuccinic acid and thiophenylphosphine derivatives.

Despite the large amount of data present in the literature on the synthesis of MPCs prepared with several thiol-based ligands, using the two phase method developed by Brust,^[4] the role played by the ligand "sulphur denticity" on the gold clusters size has not been yet systematically studied.

In this context we have recently explored the possibility to use multidentate calix[n]arene derivatives **1** and **2** (see Figure 1), characterized by the presence of two and three convergent undecanthiol chains onto their lower rim, respectively, for the preparation of Au MPCs. The particular multidentate structure of the calixarene derivatives allows the preparation of rather monodispersed clusters as shown by TEM measurements (see Figure 2) and powder XRD analysis. In particular, when the calixarene is used in excess with respect the aurate salt AuCl_4^- , clusters having a core of subnanometer size were obtained. These results open new possibilities for the synthesis of MPCs with controlled and reduced size to be employed in the emerging field of the nanotechnology.

References:

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Figures:

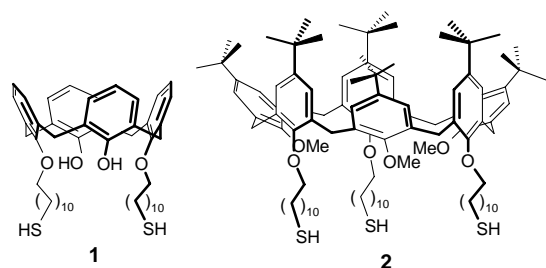


Figure 1. Polyalkylthiols lower rim functionalized calixarene derivatives for the preparation of Au MPCs.

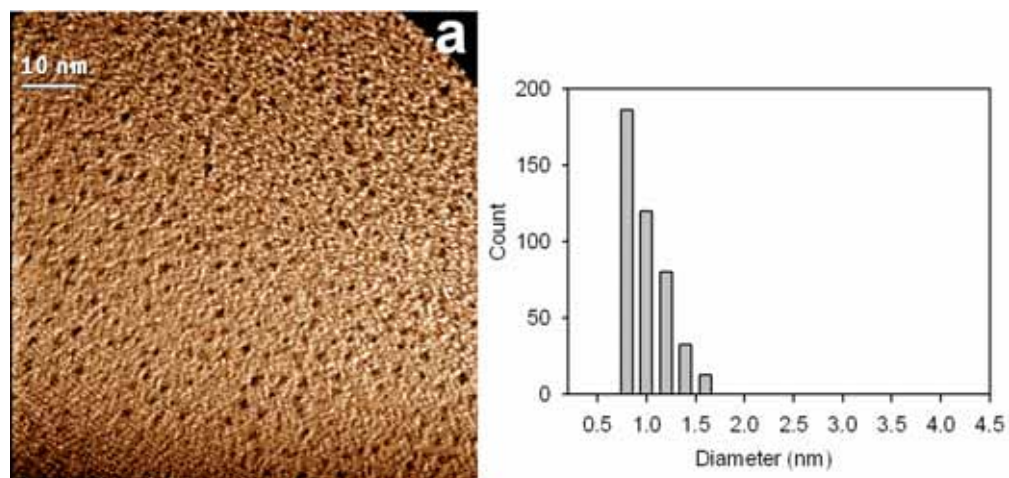


Figure 2. TEM image and core size distribution diagram of MPCs coated with calix[4]arene **1**.