MOLECULAR RECOGNITION BY CALIX[4]ARENE-MODIFIED GOLD NANOPARTICLES IN AQUEOUS SOLUTION

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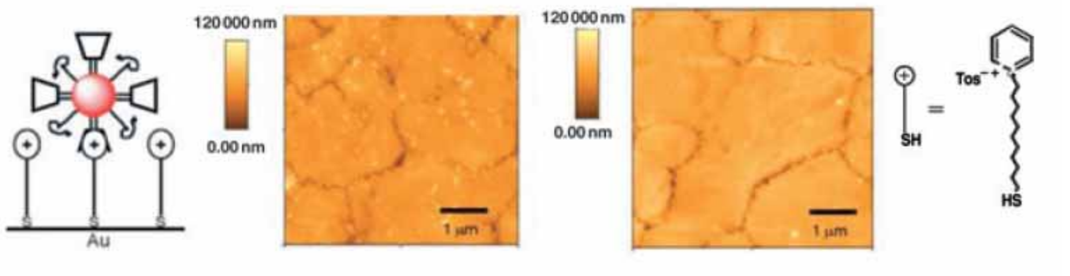
The concept of exploiting metal clusters for nanotechnology applications dates back to the development of the original Au_{55} cluster by Schmid et al. in 1981.[1] Over the past decade, so-called monolayer protected clusters (MPCs) of gold and, to a lesser extent, silver have been studied extensively owing to their extreme stability and the plethora of tunable properties that are controlled by the particle size and by the ligand chemistry.[2] The stability is usually achieved by the use of thiolate ligands, which form a protective shell around the particles to which they are attached by the strong Au–S interaction. In view of future bioanalytical applications it is desirable to develop new MPC systems that are not only stable and soluble in water, but also capable of molecular recognition in aqueous systems. Very stable, yet chemically versatile watersoluble MPCs are obtained when a sulfanylalkyl oligo(ethyleneglycol) is used as a stabilizing ligand. Herein we report the preparation and chemical properties of 14-nm gold MPCs, which are stabilized in this way and, in addition, carry in their ligand shell calix[4]arene moieties, which confer their specific molecular recognition properties to the particles. The sulfanylalkyl oligo(ethyleneglycol) ligands in the system described herein act therefore not only as stabilizers for the MPCs but also as solubilizers for the attached calix[4]arene units. The particles prepared have been characterized by transmission electron microscopy (TEM) and by UV/Vis, and NMR spectroscopy. Specific recognition of immobilized cationic pyridinium moieties by the calixarene-modified MPCs in aqueous solution has been demonstrated by atomic force microscopy (AFM).

References:

[1] G. Schmid, R. Pfeil, R. Boese, F. Bandermann, S. Meyers, G. H. M. Calis,W. A. Vandervelden, Chem. Ber., **114** (1981), 3634. [2] R. L. Whetten, M. N. Shafigullin, J. T. Khoury, T. G. Schaaff, I. Vezmar, M. M. Alvarez, A.Wilkinson, Acc. Chem. Res., **32** (1999), 397.

Figures:



Specific binding of the calixarene-modified gold nanoparticles, from aqueous solution to a self-assembled monolayer (SAM) of the pyridinium salt on a gold surface shown by AFM (left). The control experiments (right) show the nonspecific attachment of only very few particles to the SAMs.