Surface Modification of Gold Nanoparticles Using Template Controlled Ligand Exchange Reactions

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Monolayer protected gold clusters (MPC) have attracted interest in many fields of research because of easily tunable properties. Another attractive feature of MPC is that surfacebound alkane thiols can be exchanged with functionalized thiols allowing the preparation of nanoparticles with characteristic surface functionalities, so-called mixed-monolayer protected gold clusters (MMPC). Decorating MPC with suitable binding sites gives rise to synthetic receptors, for instance, whose properties are characteristically influenced by the gold core.

Exchange of thiols on the surface of a gold cluster is a reversible reaction, which proceeds under thermodynamic control. Equilibrium is thus controlled by parameters such as concentration of free thiols in solution, temperature, as well as steric and electronic effects of the substituents in the functionalized thiols stabilizing a certain MMPC surface distribution. So the distribution of functional groups on the surface of an MMPC might also be controlled by a suitable template molecule present during the ligand exchange reaction, which binds to the surface functionalities. This concept relates to the *molding* strategy in dynamic combinatorial chemistry used for the identification of synthetic receptors. If successful, this approach could extent the repertoire of reversible reactions in dynamic combinatorial chemistry and would introduce a new route for the synthesis or optimization of nano-sized MMPC-derived receptors.

This concept was evaluated on the basis of the flavine binding MMPC described by Rotello as a model system. An alkylthiol passivated gold nanoparticle was equilibrated with pyrene and diaminopyridine functionalized thiols. Ligand exchange reactions were carried out in the absence and presence template, and the resulting nanoparticles compared concerning their surface composition and binding affinities.