Physicochemical Properties of Molecular Gold Nanoclusters

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Monolayer-protected gold clusters (MPCs) are systems in which a layer of suitable ligands, usually thiolates, stabilizes and protects an otherwise reactive gold core. As the number of gold atoms decreases, MPCs start displaying a borderline behavior between that of actual molecules and larger nanoparticles. These protecting monolayers are often represented as the 3D equivalent of 2D self-assembled monolayers (SAMs) on extended gold surfaces. However, despite the growing relevance of MPCs in important applied areas, such as catalysis, sensors and nanomedicine, our knowledge of the dynamic structure of these 3D SAMs is quite limited. This is particularly true for the ultrasmall nanoclusters displaying molecular properties (gold cores of diameter <1.6 nm).

$Au_{25}(SR)_{18}$ (core = 1 nm) is a particularly stable thiolate-protected gold nanocluster that has provided and still provides the true "gold mine" for gaining insights into the properties and potential applications of molecular MPCs, as well as developing and testing new concepts at the nanoscale. We prepared a large series of monodisperse $Au_{25}(SC_nH_{2n+1})_{18}$ clusters (with n varying between 2 and 18; linear but also branched chains) and studied how the charge state affects their nuclear magnetic resonance and electron paramagnetic resonance behavior. Similarly, we studied how electrons tunnel through the corresponding monolayers. Heterogeneous electron-transfer results, nicely supported by ^1H NMR spectroscopy and molecular dynamics calculations, provided an interesting, self-consistent picture of how an ultrasmall gold core talks with the environment through/with its protecting but not-so-shielding monolayer. The distance dependence of the electron-transfer rate in solution was then compared with that of electron transfer in the solid state. These and further results concur in showing that electrochemically determined electron-transfer rates and a careful study of the clusters' magnetic properties provide the most efficient and sensitive tools for probing the solution-phase structure of the otherwise elusive 3D monolayers of molecule-like MPCs.