Combined spectroscopic studies of functionalized clusters for ion sensing

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Ultra-small thiolate-protected gold nanoclusters of the formula of $Au_m(SR)_n$ have gained tremendous interest in recent years. Several sizes have been synthesized and characterized with several physico-chemical methods [1,2]. Recently, ligand exchange reactions are commonly used for post-synthetic functionalization of gold clusters [3-5]. This reaction allows one to impart new properties to the clusters, opening the door for applications. Furthermore, the choice of ligand and control over the reaction conditions allow tailoring of optical and electrochemical properties and tuning of solubility. The aim of this research was to study the ligand exchange reaction between achiral $Au_{25}(2\text{-PET})_{18}$ and a thiolated 18-crown-6 ligand (L). The ligand contains two thiol groups, which ensures firm anchoring to the cluster. The exchanged cluster works as a potential ion sensor for K^+ and NH_4^+ present in solution even in trace amounts. The optimized reaction conditions allow to obtain several $Au_{25}(2\text{-PET})_{18-2x}L_x$ exchange species that are easily separated by size exclusion chromatography. The ion sensing was successfully achieved using 10-5000ppm KBr and NH_4Cl solutions. The reaction was followed in situ by NMR, UV-vis, HPLC and FTIR. MALDI-TOF mass spectrometry analyses show the presence of incorporated ions onto the crown ether macrocycle.

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