Impact of reduction, oxidation and ligand modification on the physicochemical properties of magic gold nanoclusters.

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In this work, we elucidate the impact of reduction and oxidation (red/ox) on the physicochemical properties of different thiolated gold nanoclusters (NC) of type $[Au_{25}(C_nH_m)_{18}]^x$ (with x=-1,0,+1) in two molecular solvents. Gold NCs have gained growing interest as building blocks for nano-clustered materials and devices due to their size specific geometry, symmetry and extraordinary high stability[1,2]. In e.g. the smallest cluster $Au_{25}(CH_3)_{18}$ an icosahedral core consisting of Au_{13} is protected by six V-shaped motifs [-S-Au-S-Au-S]. In our study, we decorate each thiolate atoms with alkyl chains of increasing length from C_4H_9, C_5H_{11} to C_6H_{13} and investigate the gas-phase and liquid properties of electro neutral, single reduced and oxidized species. It is expected that the ligand length affects the separation of the gold NCs due to different interaction strength between the ligands and the surface of HPLC column, however the influence of red/ox states of the gold NC is less studied.

Experimentally, the stability of gold NC upon ionization and reduction was proven and $[Au_{25}(CH_3)_{18}]^x$ can be obtained in the red/ox states x= -1,0 to +1. To understand the charge distribution along the NC and ligands, we conducted DFT calculations and parametrized a force field to enable the investigation of bulk and transport properties via Molecular Dynamics simulations.

We observed that the actual red/ox state has minor impact on the structural behavior of the different magic gold NCs and only the Au core is participating in the red/ox reactions. However, we observed significant charges of the liquid properties upon ligand modifications.

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2.Negishi, Y Phys. Chem. Chem. Phys. 12, 2010, 6219–6225.