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学 位 論 文 内 容 の 要 旨

DISSERTATION ABSTRACT

博士の専攻分野の名称　博士（工学）　氏名　HUANG Zhong

学 位 論 文 題 名

Title of dissertation submitted for the degree

Surface Chemistry of Cationic-Ligands-Protected Gold Nanomolecules: Ligand Exchange, Protonation, and Menshutkin Reactions on Au_{25} Cluster

(カチオン性リガンド保護金ナノ分子の表面化学:金 25 量体クラスター上でのリガンド交換・プロトン化とメンシュトキン反応)

Tailoring thiolate ligands (SR) on atomically-precise gold (Au) clusters is of great importance in the functionalization of clusters toward the rational design of their properties and applications. The pendant R-group on cluster surface is exposed to solutions and other phases, and therefore its molecular chemistry determines the molecular-like characteristics of clusters. Regarding the charge state (+1, 0 and –1) of R-group, a vast majority of $Au_n(SR)_m$ clusters have been prepared through the use of neutral and anionic SR ligands, such as phenylethanethiol, methylbenzenethiol, alkanethiols, glutathione, and mercaptocarboxylic acids, among others. There is very rare research concerning the cationic R-group. However, in some special applications, such as biological system, cationic R-groups are incorporated on the cluster surface to cater the long-held belief that these moieties would yield intimate interactions with the negatively charged contents. Based on this circumstance, this study is to explore the surface chemistry on the cationic-ligands-protected Au clusters.

Chapter One is a general introduction into the noble metal clusters with atomically precision, especially the most-widely researched $Au_{25}(SR)_{18}$. It summarizes the achievements focusing on synthesis, characterization, structure determination, surface engineering and application.

Chapter Two reports the first investigation into the kinetics of cationic-ligand-exchange processes through the reaction of $Au_{25}(SCH_2CH_2Ph)_{18}$ with a cationic thiol $HS(CH_2)_{11}N(CH_3)_3^+$, which resulted in different populations of the two thiolate ligands (SR^0 and SR^+), i.e., $Au_{25}(SR^0)_{18-x}(SR^+)_x$. It reveals that the kinetics of the cationic-ligand-exchange process, which is different from a typical neutral-thiol-to-neutral-thiol ligand exchange, is strongly dependent on how the SR^+ ligands interact with each other during the ligand-exchange process.

Chapter Three describes the first synthesis of high-purity and high-yield Au_{25} clusters protected by basic pyridyl ethanethiol ($HSCH_2CH_2Py$, 4-PyET and 2-PyET). The as-obtained $[Au_{25}(4\text{-PyET})_{18}]^-{\cdot}Na^+$ clusters show a structure similar to that known for the phenyl ethanethiolate analog, but with pyridyl-N coordination to Na^+, a more relaxed ligand shell, and a profoundly layered arrangement in the solid state. Because of the pendant Py moiety, the $[Au_{25}(4\text{-PyET})_{18}]^-$ clusters are endowed with unique (de)protonation equilibria, which results in the formation of positively-charged -Py·H^+ moieties on Au cluster surface. In addition, $[Au_{25}(4\text{-PyET})_{18}]^-$ clusters showed an unexpected H^+-dependent solubility that is tunable in aqueous and organic solvents.

Chapter Four investigates the photoluminescence (PL) properties on $Au_{25}(PyET)_{18}$ and $Au_{25}(4\text{-}PyET)_{18}$. The results showed that PyET ligand with electron-rich pydidyl-group could significantly enhance the PL emission of Au_{25} clusters. The ligand-to-metal electron transfer is responsible for the PL enhancement on $Au_{25}(PyET)_{18}$. In addition, upon involvement of the proton (H^+), the protonated PyET would reduce the electron-donation, and the emission responses of PyET-capped Au_{25} clusters were found to correlate with the resonance-coupled structure of PyET ligands.

Chapter Five investigates the Menshutkin reaction on $Au_{25}(4\text{-}PyET)_{18}$ cluster through the reaction of surface pyridyl moieties with the dimethyl sulfate, which resulted in the formation of consistently-cationized Au_{25} clusters, i.e., $Au_{25}(4\text{-}PyET\text{-}CH_3{}^+)_x(4\text{-}PyET)_{18-x}$. The results showed that the surface Py moieties amenable to be methylated into Py-$CH_3{}^+$ can easily achieve the methylation modification of PyET-capped Au_{25} clusters, which opens a facile route to allow the post-assembly of positive charges to metal clusters via interfacial surface modification.

Chapter Six summarizes the research findings, contributions and perspectives of the thesis.