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# Investigating solvent effects on aggregation behaviour, linear and nonlinear optical properties of silver nanoclusters

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We herein report the solvent effects on the aggregation, linear and nonlinear optical properties of silver nanoclusters synthesised using three solvents namely; ethanol, acetone and isopropanol. The Ag clusters were characterized using UV–Visible (UV–vis) and photoluminescence (PL) spectroscopy, Fourier transform-infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), high resolution transmission electron microscopy (HRTEM), small angle X-ray scattering (SAXS), dynamic light scattering (DLS), and open aperture Z-Scan measurements. Density functional theory (DFT) calculations at the B3PW91 level of theory, were done to compute the electric dipole, quadrupole, octapole and hexadecapole moment of mercaptosuccinic acid and mercaptosuccinic acid-$Ag_9$ cluster in three solvents. Linear optical properties show characteristic absorption profile with quantum confinement at different wavelengths for all the three clusters. The Open aperture Z-scan measurement in Ag clusters establishes the optical limiting properties which arise mostly from excited state absorption (ESA) and relatively weak saturable absorption (SA). The nonlinear optical behaviour varies within the three clusters with maximum optical limiting value obtained for the clusters synthesised using acetone. The theoretically computed hyperpolarizabilities together with z-scan measurements establish the solvent effect on the clusters and their potential applications in optical limiting devices.



## 1. Introduction

Noble metal nanoparticles and quantum clusters (QCs) are of great importance nowadays because of their applications in the field of optoelectronic, nonlinear optical, electrical, magnetic, medicinal, catalytic, sensing and environmental applications [1–5]. Nanoclusters or quantum clusters (QCs) are extremely small-sized particles (from sub nanometer scale to < 2 nm) which proceed as a bridge between atoms and nanoparticles. They exhibit unique physicochemical properties because of the enormous changes in size and atomic structure arrangement in this size regime [6]. Metal QCs which are protected by thiolate ligand groups can control the number of metal atoms in the cluster which are stable and exhibit molecular-like properties [7]. When the size of the clusters is comparable to the Fermi wavelength, the properties are governed by quantum confinement effects (HOMO-LUMO bandgap) that

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results in discrete energy levels. Noble metal clusters are found to be good candidate for sensing, catalytic and nonlinear optical applications [8–10]. Among these noble metal clusters, Au nanoclusters are the widely studied [11,12]. The studies on Ag nanoclusters are of immense interest and have been investigated intensively because of their comparable properties with Au quantum clusters and enhanced optical, nonlinear optical, sensing, biolabelling and catalytic properties [13–17].

Different protocols have been reported for the synthesis and characterization of stable Ag and Au nanocluster molecules [18,19]. The most common methods for the synthesis of silver clusters are ripening [20], core etching [21], high temperature [22], solid state [23], gel mediated [24], interfacial [25], reversible phase transfer [26] and some traditional routes [27] such as cyclic reduction in oxidative conditions (CROC) in aqueous solutions. Douglas R Kauffman et al. synthesised ligand-protected mixed-metal $Au_{25-x}Ag_x(SR)_{18}$ clusters having charge dependent optical properties and oxidative photoluminescence quenching [28]. Indranath et al. synthesised Polyethyleneimine (PET)-templated icosahedral silver quantum clusters using a solid state route and found the cluster to be superstable [29]. Polyethylenimine-capped silver nanoclusters has been reported for selective sensing of halide ions and as colorimetric pH sensor [30,31]. This type of pH sensors with nano dimensions would be a good candidate for biological, medical and pharmaceutical applications. Jun Lu et al. have investigated the effect of size selective silver clusters on discharge product morphology in lithium-oxygen batteries. This helps to explore the detailed mechanism of charge and discharge process and hence an understanding of how to control this electrochemical processes [32].

The effects of solvent on the physicochemical properties of clusters especially of linear and nonlinear optical properties are not much reported. Isabel Diez et al. [33] have reported the strong solvato-chromic and solvato-fluorochromic properties of Ag nanoclusters, which can be used as molecular sensing probes. Kumaranchira R. Krishnadas et al. [34] reported the synthesis of AgAu alloy quantum clusters, which shows selective quenching of cluster luminescence by addition of $Cu^{II}$ ions which can be tuned by using different solvents and ligands. The major characterization techniques used to analyse the metal clusters are UV–Vis, PL, XPS, elemental analysis, mass spectroscopy, FT-IR, $H^1$ NMR, TEM, and recently crystallographic data, which helps to elucidate and understand their fundamental properties. For instance, in the TEM investigation, high energy electron beam radiation onto the clusters has been reported to cause electron-beam-induced coalescence of the clusters to nanoparticles which in turn affect the physico-chemical properties of the clusters [35–37]. In addition, these aggregates may become twinned, and may have stacking faults or various types of defects. To elucidate and understand the fundamental process of aggregation, the combined methods of TEM, SAXS, SANS, DLS, UV–Vis, XRD and kinetic modelling are commonly used [38,39].

Linear and nonlinear optical (NLO) properties of Ag clusters are of significant importance nowadays due to their marked applications in the field of optoelectronic devices [40,41]. Sadia Afrin Khan et al. have investigated theoretical and experimental values of absorption maxima and static first hyper-polarizabilities $\beta$ of $Ag_n$ ($n$ = 10, 20, 35, 56, 140, 980) for linear and nonlinear optical properties and understand that the NLO properties can be improved by controlling the cluster size [42]. Their data shows that $\beta = 4.8 \times 10^{-28}$ esu for $Ag_{980}$ quantum clusters, is having the highest $\beta$ value compared to others. Stefan Knoppe et al. [43] used density-functional theory to examine the static first hyper-polarizabilities $\beta$ of the clusters $[Au_m(SH)_n]^z$ (m = 18–38). They found that, there is no correlation between cluster size and $\beta$; however the NLO properties are governed by the symmetry of the clusters. Reji Philip et al. [44] investigated the discrete evolution of the optical nonlinearity as the gold atomic clusters grow in size from the non-plasmonic regime to the plasmonic regime. Their study showed that, at the SPR wavelengths of noble metals, the quantum clusters are better candidates for optical power limiting applications, since the absorption saturation effects are absent at these excitation wavelengths. Paul N. Day et al. [45] applied density functional theory (DFT) and time-dependent DFT (TDDFT) on thiolated silver nanoclusters $[Ag_{44}(SR)_{30}]^{4-}$, $Ag_{14}(SR)^{12}(PR'3)^8$, $Ag_{31}(SG)_{19}$, $Ag_{32}$-$(SG)_{19}$, and $Ag_{15}(SG)_{11}$] and hence calculated the linear and nonlinear optical properties such as one-photon absorption (OPA) and two-photon absorption (TPA).

Novel optical limiter materials investigations are of primary importance for protection from laser light to human eyes and for sensitive optical instruments. In an optical limiter, as the input light fluence increased, the optical transmittance is largely reduced. Philip et al. reported that a significant enhancement of the optical limiting efficiency occurs in Au clusters compared to Au NPs due to the absence of surface plasmon resonance in Au nanoclusters [44]. Sridharan et al. also reported enhanced optical limiting efficiency for $Ag_9$ quantum clusters and its graphitic carbon nitride nanosheets composite [46]. In another development, Rao et al., synthesised $Ag_9$ quantum clusters using different synthetic conditions and solvents such as ethanol, methanol, DMF, $H_2O$ and DCM and found that different solvents give different linear optical properties [23]. However, the studies on the effect of different solvents on the nonlinear optical properties of Ag quantum clusters are still lacking. In this article, silver nanoclusters consisting of Ag atoms core protected with mercaptosuccinic acid ($H_2$MSA) have been synthesised by using three different solvents; namely ethanol, acetone and isopropanol. The solvent effect on various properties, such as aggregation, linear and nonlinear optical effects of the clusters was investigated using UV–Vis, PL, XRD, SAXS, TEM, DLS, RAMAN, FT-IR and XPS while open-aperture Z-scan technique was used to investigate the solvent effect on the nonlinear optical properties. These investigations will help in the clear understanding of NCs properties and hence can be used for the fabrication of novel and functional materials for different applications.

Investigating the linear optical and nonlinear optical properties of silver clusters in different local environments suggests its potential use in chemical, biological sensing and optical limiting applications. A few studies have been done by researchers for tuning the Ag clusters properties by changing the local environment. Isebel Diez et al. [33] for the first time demonstrated that the chemical environment such as solvent can dramatically change the optical properties of silver nanoclusters. The cluster shows strong solvatochromic (solvent dependent shift of the spectrum), solvatofluorochromic and electrochemiluminescence properties, which can be used in molecular sensing applications. Isebel Diez et al. [47] also reported the synthesis of blue, green and red emissive silver clusters in different organic solvents and the shift in emission band with respect to excitation wavelength are explained as structural inhomogeneiy of clusters. Pradeep et al. [48] suggested that the increase in luminescent intensity was due to the reduced hydrogen bonding between silver nanoclusters and the solvent molecules. Yang Li et al. [49] studied the solvent effect on the luminescence of silver nanoclusters. They consider the effect of solvent on to the protecting ligand around silver nanocluster. U. Reea Felscia et al. [50] investigated the linear and nonlinear properties of Pyrene adsorbed silver cluster. Herein we have investigated the effect of solvents on the physico-chemical properties of Ag nanoclusters in three polar solvents by experimental and computational methods. We have synthesised the water soluble clusters, and selected the polar solvents, ethanol, acetone and isopropanol such that it should