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Metal Nanoparticles

Silver Nanoparticles with Broad Multiband Linear Optical Absorption**

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The optical and electronic properties of metal nanoparticles (NPs) have made them ideal for applications in many fields such as bioscience,[1–3] nanophotonics,[4] and nanoelectronics.[5,6] Silver NPs have attracted large research efforts as their properties strongly depend on the particles' size,[7–9] shape,[10,11] surrounding medium,[12] and aggregation state.[11] It is accepted that small silver clusters (up to about 8 atoms) have molecule-like optical transitions with absorption bands that depend on the number of atoms that compose the cluster and with a bright fluorescence emission.[13,14] Clusters of up to 21 atoms exhibit one or more photoabsorption maxima.[15] As particles grow (size ≥ 2 nm), they lose these properties and develop an optical absorption band that depends on the surface plasmon resonance of their free electrons—the larger the particles the stronger the resonance.[8,16] The jellium model[7] and time-dependent density functional theory calculations[17] have been used to explain the molecule-like state, whereas classical electromagnetic theories and methods, such as Mie theory, have been proven to be adequate in modeling the optical properties of larger particles.[9,18] Herein we show that it is possible to create aryl thiol coated silver NPs that show intense and broad non-plasmonic optical properties at an intermediate size. These particles have eight distinct absorption bands covering the entire visible spectrum with extinction cross-sections as high as $2.59\times10^5\,\mathrm{L\,mol^{-1}\,cm^{-1}}$. They are relatively stable and upon heating grow into larger NPs with plasmon-like absorption. These particles have a predominant size ($d_{\mathrm{core}}\approx 1.3$ nm) and a highly defined structure in their optical spectra. Ab initio calculations for a quantum confined aryl thiolate silver cluster structure reproduce the complexity of the spectra observed and point to a significant molecular nature of the observed transitions. These intensely and broadly absorbing nanoparticles (IBANs) have larger cross-sections than conventional organic dyes and inorganic QDs, and cover a broader range of wavelengths (their absorption bands cover the range 380–850 nm). These properties make IBANs ideal candidates for light-harvesting applications.

Recently, a few groups reported the structure determination of small (≤ 2 nm) gold NPs.[19–22] These NPs, which are far larger than the clusters mentioned above, show a unique structure of both their core metallic atoms and of their aryl thiol ligands.[19–22] In addition to their unique structural motif, some of these gold particles exhibit molecular steplike transitions in their absorption spectra.[19,22–27] Similarly sized particles coated with other thiols,[25–28] whose structures have not yet been determined, also show these steplike transitions in their linear optical spectra. However, the steplike behavior becomes less resolved as the clusters grow in size or become less monodisperse.[29–31] A couple of reports on silver NPs (size <2 nm) have shown very broad steplike optical transitions, whose characteristics are hard to discern even in the first derivative of the absorption spectra.[32,33] The particles reported herein (IBANs) are the first silver nanoparticles to show strong and complex molecular-like absorption peaks that are markedly different from those previously reported for either silver clusters or silver NPs, even when they are similarly sized.[16,33,34]

IBANs were prepared through the reduction of a silver salt solution in the presence of the capping ligand 4-fluorothiophenol (4FTP) in a procedure that deviates from the usual one-phase[35,36] NP synthesis (see the Supporting Information). In a typical reaction, 4FTP was stirred with a silver salt (4FTP:Ag = 2:1) in *N*,*N*-dimethylformamide (DMF) for 15 min. A solution of $NaBH_4$ in DMF ($NaBH_4$/Ag = 4:1) was then added to the reaction vessel, after which the solution turned brown and darkened further with time. The observation of a plasmon-like absorption band at about

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$\lambda = 450$ nm presumably indicates the formation of silver NPs at this stage. The reaction mixture was left to stir for 4 h until the color of the solution faded to transparent yellow. The decay of the plasmon-like resonance indicates that particles have either been digested back into seeds or disassociated completely into silver ions or into the layered compound that is known to be an intermediate precursor for the synthesis of silver NPs.[37] A small amount of water was added, increasing the reducing power of $NaBH_4$. Within minutes, the reaction color began to darken again. A broad peak centered around $\lambda = 490$ nm formed. The reaction was left in the freezer (−4 °C), whereupon reduction occurred over several days. In that time, the single broad peak began splitting into multiple narrow peaks (see Figure S1 in the Supporting Information). The spectrum stopped evolving within less than a week from the start of the reaction. The final color of the solution was pink and remained stable in the freezer for at least 18 months without further manipulation. For further characterization, the NP solution was filtered using gel permeation chromatography. One of the main impurities at this stage was the layered compound, which we confirmed by powder X-ray diffraction[38] and by its well known optical signature.[39,40] The filtered and hence purified solutions are stable for many weeks at room temperature in an inert atmosphere or for several days in ambient air. The UV/Vis absorption spectrum of IBAN solution is shown in Figure 1 a. The spectrum exhibits six pronounced and two weak peaks. Table S1 (in the Supporting Information) lists the major peak positions averaged from 20 different synthesis batches. The very small standard deviation (1.7 nm on average) in peak positions attests to the excellent reproducibility of our synthesis method.

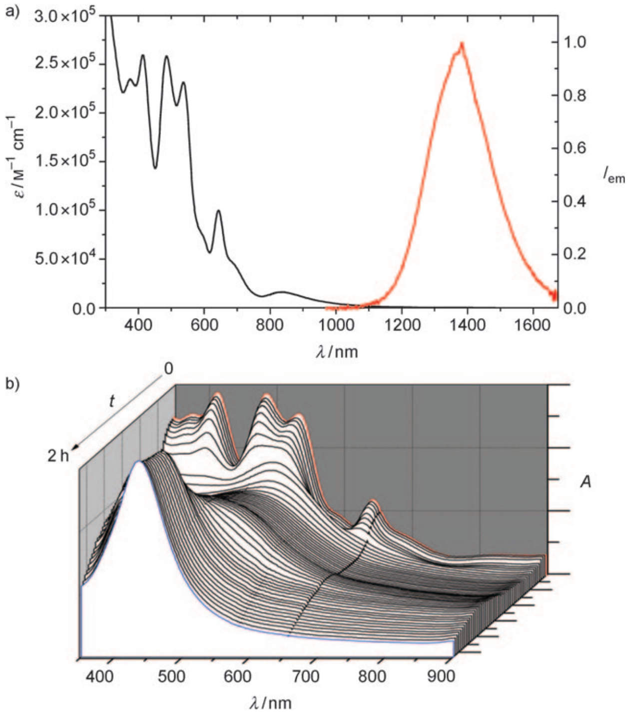

Figure 1. Optical spectra of a solution of IBANs in DMF. a) The UV/Vis/NIR spectrum (black) shows multiple strong absorption peaks and a single IR emission band (red; quantum yield in DMF ca. 0.01 %). b) UV/Vis/NIR absorption spectra of an IBAN solution heated at 90 °C and monitored over time. The NPs were IBAN initially (red line) but were transformed into larger NPs with a single plasmon-like resonance (blue line).

We have determined that several conditions are needed to obtain IBANs (Figure 1 a) instead of larger NPs with a single plasmon-like absorption peak. First, the molar ratio of thiol molecules to Ag should be 2:1. A higher amount of silver results in the formation of a mixture of both IBANs and larger plasmon-like NPs, with the fraction of plasmon-like NPs increasing with increasing amounts of the starting Ag salt. Increasing the amount of ligand results in an overall decrease in the yield of IBANs (without introducing plasmon-like NPs). At a thiol/Ag ratio of 4:1, the yield of IBANs was too low to detect with UV/Vis spectroscopy. Others[41] have observed a similar trend in some syntheses of thiol-protected palladium NPs, which exhibited two nonplasmonic absorbance peaks only when the thiol/Pd ratio was greater than or equal to 2:1. Second, a small excess of $NaBH_4$ is needed so that the plasmon-like NPs formed at the beginning are eventually digested. Finally, the end product is very sensitive to the temperature at which the final reduction occurs. Freezer temperatures (−4 °C) were necessary to obtain IBANs. Leaving the reaction at higher temperatures produced only plasmon-like NPs, likely because the reduction occurs too quickly.

Our initial investigations of IBANs were centered on proving that the unique optical spectra that they show was due to a single type of particle present in solution and not some form of impurity. The complexity of the absorption spectrum (Figure 1 a) may raise the question as to whether more than one type of NP or absorbing species is contributing to the spectrum, for example, a cocktail of small silver clusters. We monitored the absorption spectrum of an IBAN solution subjected to intense (30 mW) laser irradiation ($\lambda =$ 521 and 647 nm). We found that the optical spectra slowly bleached to decay into the spectrum of the layered compound; more importantly, all the bands bleached at what appears to be the same rate independently of the irradiation wavelength (Figure S3 in the Supporting Information); the most reasonable explanation for this behavior is that all the bands belong to one absorbing species. Furthermore, the excitation of IBANs at different peak wavelengths resulted in the same emission spectrum centered around $\lambda = 1375$ nm (Figure S2 in the Supporting Information). Finally, the peak positions and more importantly the intensity ratios in the absorption spectrum were always approximately the same regardless of synthesis batch (Table S1). Figure S4 (in the Supporting Information) shows the absorption spectrum (in the solvent in which they were synthesized) of three IBAN samples synthesized in three different solvents: DMF, THF, and ethanol. Despite the differing synthesis conditions and solvent, the peak positions and relative intensities were virtually unchanged. These data imply that the observed spectrum depends on either a single NP species or different NPs with only slightly different absorption spectra, leading to optical behavior very similar to that of the monodisperse case.

We performed a series of studies (and finite-difference time-domain electrodynamic simulations) to understand whether the optical response of the IBANs could be plasmonic in nature. We ruled out this possibility because the spectrum has minimal to no response to variation in refractive index of the surrounding medium, and cannot be reproduced by simulations of a truly large variety of particles varying in shape and size. Moreover, as stated above, the excitation of IBANs results in an emission centered around $\lambda = 1375$ nm (Figure 1 a). This emission is uncharacteristic of plasmonic NPs and is more red-shifted than previously reported luminescence from silver NPs or clusters.[34,42–44] These data suggest that the optical transitions observed for IBANs are not plasmonic. We heated a solution of IBANs in DMF at 90 °C and monitored its absorbance spectrum over time (Figure 1 b). After about 2 h we found the spectrum evolved into a single plasmon-like resonance at $\lambda \approx 440$ nm. We calculated the molar extinction coefficient of the IBANs (Figure 1 a) by carefully measuring the absorbance of solutions containing a known amount of NPs of a known diameter (as estimated by XRD and ultracentrifugation, see below). We found that all the molar extinction coefficients (ε) of peaks below $\lambda = 550$ nm were greater than $2 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$, and even the weakest absorption peak at $\lambda = 839$ nm had an ε value of $1.63 \times 10^4\,\text{M}^{-1}\,\text{cm}^{-1}$.[45,46] For a point of reference, the metal-to-ligand transition of the Ru K19 dye used in solar cells has an ε value of $1.82 \times 10^4\,\text{M}^{-1}\,\text{cm}^{-1}$ at $\lambda_{\text{max}} = 543$ nm.[45,46]

We employed several direct and indirect methods to estimate the size and distribution of IBANs. Information on the size of the IBANs and the NPs with the plasmon-like absorption was obtained by ultracentrifugation[47,48] of the particles in DMF with a density gradient of either sucrose or deuterated DMF (see the Supporting Information). The sedimentation coefficient of IBANs (3.5 ± 0.3 Svedberg) is consistent with a core size in the range of 1.24 ± 0.23 nm (see the Supporting Information). The majority of NPs with plasmon-like absorption at $\lambda \approx 440$ nm have a sedimentation coefficient of 9.5 ± 0.5 Svedberg, showing that they are significantly heavier (core size estimated to be 2.1 ± 0.2 nm) than the IBANs. There appears to be a significant gap in size between the IBANs and the smallest plasmon-like NPs.

Large-angle powder X-ray diffraction (XRD) was employed to investigate the core size of the IBANs further. We followed the well known Scherrer[30,49] method to determine the size of an IBAN batch of particles, which according to ultracentrifugation results was largely free of larger plasmon-like NPs (Figure S6c in the Supporting Information), and obtained a core diameter of approximately 1.3 nm (Figure S7 in the Supporting Information). This estimate is in very good agreement with the estimates obtained from ultracentrifugation.

Proton NMR spectroscopy is a valuable tool to study the ligand shell on clusters and nanoparticles,[50] but requires solutions of very high NP concentrations and purity. For this purpose (and subsequent electrophoresis measurements), we found it advantageous to work with water-soluble 4-mercaptobenzoic acid (4MBA) IBANs instead of the 4FTP-IBANs discussed so far. Compared with 4MBA in solution, the ^{1}H NMR signal of 4MBA-IBANs is broadened and weakened (Figure S8 in the Supporting Information), but not completely suppressed, which suggests that the IBANs are likely to be smaller than 2 nm.[50–53] A qualitative comparison to the spectra that Price and Whetten obtained for anionic benzenethiol protected Au_N clusters ($N = 44$, 110, 144) reveals no direct analogue to the proton signal of the 4MBA-IBANs.[51–53] The weakening of the ligand signal in the IBANs is consistent with that observed in Au_{110} and Au_{144}, that is, 1.5 and 1.7 nm cores. However, all the dominant aromatic proton resonances in the IBANs are contained within a narrow 0.6 ppm range (Figure S8 in the Supporting Information), whereas in gold the resonances broadened over a range of 2 ppm,[51–53] owing to multiple binding sites on magnetically inequivalent or chemically different sites. On IBANs, a narrow range of dominant resonance modes is consistent with thiols binding to sites with similar local environments. In addition, the 4MBA-IBAN signal is up-shifted relative to the pure 4MBA signal (Figure S8 in the Supporting Information), which would be consistent with the 4MBA being proximal to an oxidized metal moiety.[53] These two observations suggest qualitatively that 4MBA is on an Ag^{I} layered thiolate complex[38] or on NP cores protected mostly by RS-Ag-SR staple motifs (see Figure 2 a as an example), which is a ubiquitous structural element in many

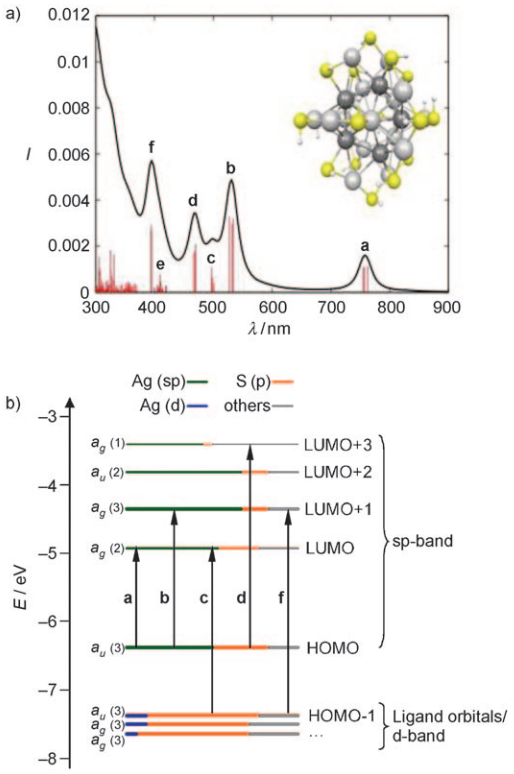

Figure 2. a) Theoretical absorption spectrum of $[\text{Ag}_{25}(\text{SH})_{18}]^-$. Inset: View of $[\text{Ag}_{25}(\text{SH})_{18}]^-$ showing a fivefold coordinated facet of the icosahedral core in the cluster. Ag gray, S yellow, and H white. The Ag atoms of the fivefold facet are highlighted in dark gray. c) Theoretical orbital energy level diagram for the model compound $[\text{Ag}_{25}(\text{SH})_{18}]^-$. Each MO is drawn to indicate the relative contributions (line length with color labels) of the atomic orbitals of Ag (6sp) in green, Ag (5d) in blue, S (3p) in orange, and others in gray (those unspecified atomic orbitals, each with < 1 % contribution). The left column of the orbital shows their symmetry (g, u) and degeneracy (in parenthesis); the right column shows the HOMO and LUMO sets.

small thiol-protected gold NPs.[19,21,22,54] The insolubility of the layered complex in most solvents prevented its characterization with NMR spectroscopy. All these assumptions need to be confirmed by a total crystal structural determination of the IBANs, which the use of 4MBA ligands will facilitate.[21]

We first suspected the anionic nature of IBANs, regardless of their thiol protecting ligand, when it was noticed that they would quickly degrade in nonpolar and weakly polar solvents in the absence of a positively charged surfactant in solution (see the Supporting Information). We tried using gel electrophoresis to separate 4MBA-IBANs from larger NPs on the basis of charge and size. This method has already been proven to be successful in various NPs and small clusters.[32,33,55] 4MBA NPs were prepared in the IBAN state, single plasmon-like absorption-band state and various intermediate states by controlling the heating and amount of $NaBH_4$ in solution (Figure S9 in the Supporting Information). The IBANs and larger NPs with plasmon-like absorption moved as a single band with differing mobilities. IBANs were more mobile than plasmon-like NPs (Figure S9). Solutions prepared in intermediate states separated into two bands, one closer in character to IBANs and the other closer to the plasmon-like NPs. This result further indicates, just as the ultracentrifugation did, that IBANs are dominated by a single size. We also separately measured the zeta potential of the IBANs and larger NPs with plasmon-like absorption and found that the IBANs were more negatively charged ($\zeta = -58.7 \pm 2.6$ mV) than the plasmon-like NPs ($\zeta = -36.1 \pm 0.5$ mV), which also seemed to suggest that the differences in their gel mobilities stems also from their increased surface charge density and not just from size differences. We tried running our gels using sodium dodecyl sulphate (SDS), as some reports[33] suggest it reduces the charge contribution and makes the mobility reflect the size of the species. This had no effect in our case since SDS did not favorably interact with 4MBA-IBANs. It should be noted that significant error can be expected in zeta-potential measurements, since we are measuring particles at the size limit of the potentiometer.[55]

To correlate qualitatively the structure of the NP with its optical properties and to illustrate further the similarity between the origins of the optical behavior of previously reported gold clusters[22,29–31,60–64] and our IBANs, we performed time-dependent density functional theory (TDDFT) calculations of the electronic structure and optical spectrum of a cluster of $[Ag_{25}(SH)_{18}]^-$. This structural model is equivalent to a model of $[Au_{25}(SH)_{18}]^-$ previously used to explain the optical properties of phenylethanethiol-capped Au_{25} clusters.[22] Briefly, the cluster is centered on an Ag_{13} icosahedral core (Figure 2a). The icosahedron has 20 triangular Ag_3 faces, and the remaining 6 pairs of silver atoms cap the faces around each 2-fold axis, leaving 8 Ag_3 faces of the icosahedra uncapped. Eighteen thiolate ligands bridge the exterior Ag–Ag pairs and exterior Ag–icosahedral Ag pairs, forming S-Ag-S-Ag-S staple structures. We found this model attractive because it contains a thiol–metal–thiol structural motif that has been observed to be ubiquitous in small gold NPs.[19,21,22,54] Thus, although there is no evidence for 25-atom clusters in the results, one could imagine that larger structures with similar bonding motifs (larger cores with oligomeric Ag–S staples) might account for the observed spectra.

Remarkably, the TDDFT results (Figure 2a) for $[Ag_{25}(SH)_{18}]^-$ qualitatively reproduce the kind of optical transitions present in the experimental spectrum of the IBANs (Figure 1a). The onsets of absorption in the theoretical and experimental spectra are both roughly at 1.5 eV, which is within the energy range expected from silver NPs and clusters.[8] In Figure 2b we plot an energy diagram of the molecular orbitals (MOs) responsible for the optical transitions observed in the theoretical spectrum along with the contribution of each atomic orbital (ligand and metal bands) to the MO. All the MOs have strong sulfur character. The triply degenerate HOMO−1 in particular is dominated by the sulfur ligand along with a small contribution from the silver d band. One can see from the diagram that the low-energy optical transitions are due to intraband sp→sp transitions, whereas the higher-energy transitions are dominated by interband ligand/d-band→sp-band transitions. These results are similar to those previously found for $[Au_{25}(SH)_{18}]^-$ [22] (and indeed there are analogies between the spectra measured for that complex and that found in the present experiments), but gold shows more important d-band contributions because of the closer overlap of the d-band and sp-band energies.

For both silver and gold complexes, the strong splitting in the LUMOs of the sp band seems to be responsible for the multiple peaks in the absorption spectrum.[65] These levels are known to be sensitive to the lattice structure of the nanocrystal,[30,66,67] and indeed we expect that the size of the splitting of the LUMOs would be highest for a quantum confined structure,[60,66,68] such as the icosahedral core of the 25-atom silver cluster.

The theoretical results indicate a significant sulfur contribution to all the MOs responsible for the optical transitions, which suggests that changes to the charge density of the sulfur atom may result in perturbation to the MOs. To illustrate this situation, IBANs with 2-fluorothiophenol (2FTP) and 3-fluorothiophenol (3FTP) were synthesized and their spectra were compared to that of 4FTP IBANs (Figure 3). 3FTP and 4FTP IBANs showed near identical spectra. Only 2FTP was blue-shifted and showed different relative peak intensities. We include in Figure 3 the spectra of IBANs synthesized from

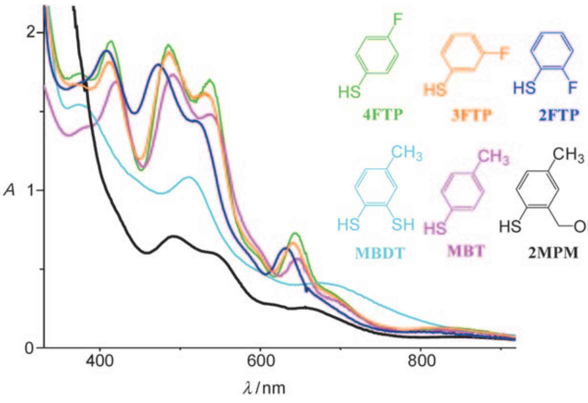

Figure 3. UV/Vis absorption spectra of IBANs synthesized using different aryl thiol ligands in DMF.

several other ligands to show that the absorption features are mostly governed by the structure of the metal core and the thiol–silver interaction, further confirming the results of our computational model and the observations of others for gold clusters.[69] We note that large deviations from the original spectrum occur only when groups are present close to the metallic surface, as is the case for 2FTP, (2-mercapto-5-methylphenyl)methanol, and 4-methylbenzene-1,2-dithiol. These results illustrate the importance of the sulfur–metal bond in contributing to the absorption spectra. At present our working explanation for the nature of the observed optical transition is based on the presence of a specific surface structure at the organic–inorganic interface in our particles, of the type that has been observed on self-assembled monolayers on gold surfaces[70] and on gold nanoparticles.[19–22]

In conclusion, we synthesized silver NPs with unique optical properties. Our work points to the importance of the surface structure in determining the electronic properties of the NP. The NPs show multiple sharp molecular-like transitions. Electronic structure calculations reproduce the complexity of the observed spectra very well and point to a molecular nature of the transitions with a significant sulfur-derived component in many of the spectral peaks. The thermally induced transformation in the IBANs presents a rare opportunity to study the transition from molecular-like behavior to bulk in Ag NPs. The synthesis of IBANs with 4MBA ligand is likely to facilitate their crystallization and full structural determination just as it did for $[Au_{102}(4MBA)_{44}]$.[21] It is apparent that IBANs are a new class of strongly absorbing broad-spectrum NP-based dyes that could find use in many applications.

Experimental Section

Experimental details of the synthesis of IBANs and characterization methods, as well as supporting figures and tables are available in the Supporting Information.

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