



Acridinedione-functionalized gold nanoparticles and model for the binding of 1,3-dithiol linked acridinedione on gold clusters

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ABSTRACT

The design and synthesis of 1,3-dithiol linked acridinedione functionalized gold nanoparticles (**ADDDT-GNP**) is described. **ADDDT-GNP** was characterized by transmission electron microscopy (TEM), Fourier transform infrared (FT-IR), UV–vis, steady-state and time-resolved fluorescence techniques. Conformational analysis of 1,3-dithiol ligands using density functional theory (DFT) reveals that they can cap on gold clusters through 1,2-capping mode, in which the two sulfur atoms of the dithiol bind covalently with two adjacent gold atoms on the surface of the cluster. The present study shows that three conformers of the ligand can cap in the 1,2-mode of capping. The triexponential fluorescence decay observed in the capped nanogold complex with fluorophore-labeled 1,3-dithiol may originate from the three conformers of the complex in the 1,2-capping mode.

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Metal nanoparticles play an important role in many different areas such as electronic, magnetic, catalysis, and biology.^{1,2} They have also been widely exploited for their use in catalysis,³ biological labeling,⁴ photonic,⁵ optoelectronic,⁶ and information storage devices.⁷ Various organic and biological sulfur-based compounds^{8,9} are used to functionalize the gold nanoparticles. Mirkin and co-workers reported that the use of multithiolated species improves the stability of colloid gold nanoparticles.¹⁰ The remarkable properties associated with nanoparticles can be rationalized, if the behavior of quantum-confined electrons in the nanometer scale is explored.^{11,12} Gold nanoparticles are stabilized through capping with a wide variety of organic ligands such as amine, thiol,^{8–10} dithiol, etc. A number of studies have investigated the nature of bonding between the nanometal and the ligand molecules.^{13–21} The metal–ligand interactions in the organic-capping layer play a crucial role in the high performance materials.^{22–25} In the recent years, several studies have been focused on the sulfur–gold bonding in alkanethiol self-assembled monolayers on Au(111).^{23–33} However, the exact nature of the S–Au bond is still debated. In the case of dithiol ligands, it is found that gold nanoparticles are bound by both sulfur ends.²¹

In this work, we have synthesized the **ADDDT-GNP** (Scheme 1), with a fluorophore-labeled acridinedione derivative of 1,3-dithiol (**ADDDT**) and they were characterized. In order to understand

the nature of bonding between the ligand sulfur atoms and the gold atoms in the capping layer, we have performed a simple modeling of the complex formation of 1,3-dithiol on gold cluster. We have examined in detail the different conformations of the simple 1,3-dithiol (1,3-dimercaptobutane) (**DTDMB**) and its molecular complex with gold atoms **Au-DTDMB** by density functional theory (DFT) calculations using B3LYP functionals.^{33,34} We have also studied the conformations of **ADDDT**, and its gold complex **Au-ADDDT**. Based on the inferences of the conformational study, the capped complexes **Au-cap-DTDMB** are modeled using the ligand **DTDMB** in a cluster of eight Au atoms. The DFT predictions are corroborated with the experimental findings.

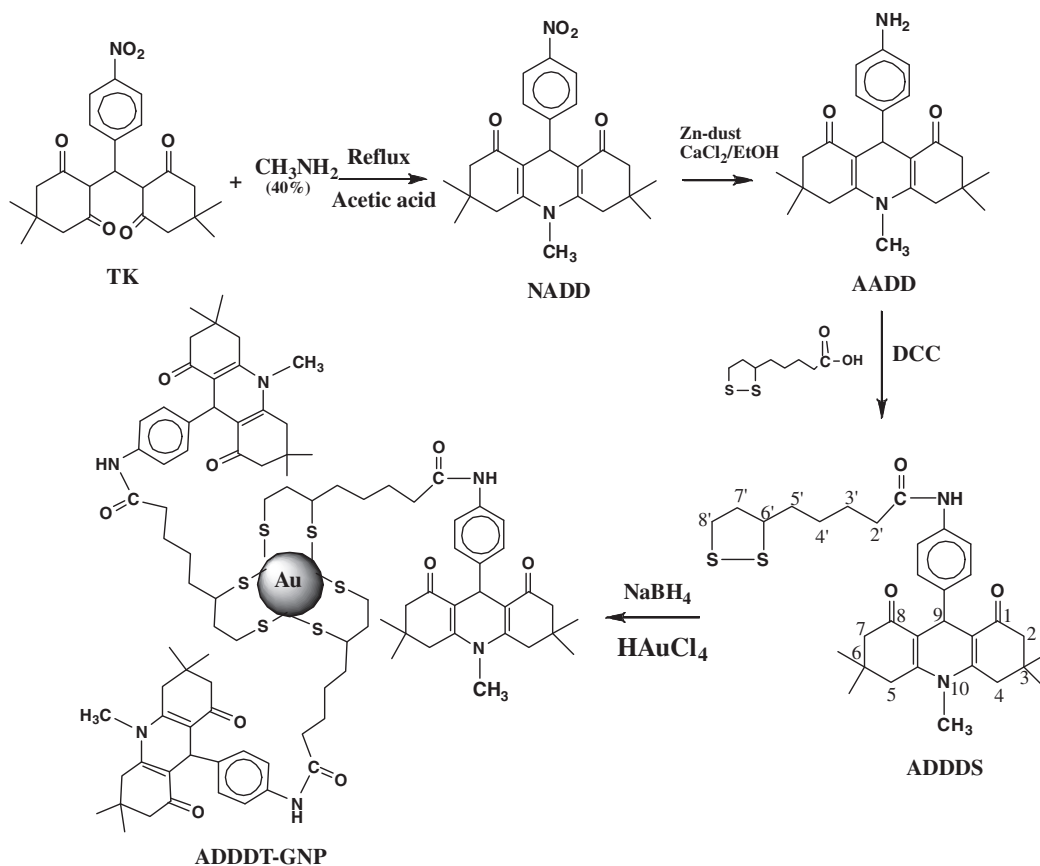
The synthesis of acridinedione disulfide (**ADDDS**), (precursor of **ADDDT**) and the **ADDDT-GNP**, were carried out as outlined in Scheme 1. Nitroacridinedione dye (**NADD**) was synthesized from tetraketone (**TK**) using the procedure reported in the literature.^{35,36} Refluxing a mixture of **NADD** with Zn and CaCl₂ in ethanol yielded the aminoacridinedione (**AADD**). An equimolar mixture of **AADD** and α -lipoic acid in dry dichloromethane in the presence of dicyclohexylcarbodiimide (DCC) on refluxing, afforded the **ADDDS**. Synthesis of gold nanoparticles functionalized with **ADDDS** was carried out by a modified procedure involving the biphasic synthesis reported¹⁵ by Brust et al. The details of the synthesis and characterization of acridinedione derivatives and its functionalized gold nanoparticles are given in the Supplementary data (Fig. S1 and S2).

The synthesized **ADDDT-GNP**, and **ADDDT**, were characterized by IR and ¹H NMR spectral studies. IR spectrum of the **ADDDT-GNP** showed no S–H stretching band. **ADDDT** showed the S–H

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stretching vibration band at 2560 cm^{-1} . The computed S–H stretching frequencies for the dithiol conformers **ADDDT** a–f at B3LYP/6-31G* level are in the range of $2567\text{--}2581\text{ cm}^{-1}$ and are in good agreement with the experimental value of 2560 cm^{-1} . In the ^1H NMR study of the **ADDDT-GNP**, multiplicity of S–CH (C6') and S–CH₂ (C8') are shifted towards up-field as compared with **ADDDS**. The IR and NMR spectral studies confirm S–Au bond formation in the **ADDDT-GNP**.²⁰

The HR TEM image was recorded by drop-casting a dilute suspension of **ADDDT-GNP** on a carbon-coated copper grid and the images are presented in Figure 1. Three-dimensional approach in TEM images indicates that **ADDDT** is anchored on the surface of

the gold nanoparticle (GNP). The GNP is found to have an average diameter of 2.5 nm and a total surface area of 19.625 nm^2 .

The absorption and emission maxima of acridinedione dyes are centered around 380 and 430 nm, respectively.^{35,36} The peak at 380 nm is attributed to the intramolecular charge transfer (ICT) from nitrogen to carbonyl oxygen in the acridinedione moiety, and the emission at 430 nm to that of the local excited (LE) state. Absorption spectrum of **ADDDS** is centered around 365 nm as shown in Figure S3 (see in Supplementary data) and the absorption spectrum of **ADDDT-GNP** (Fig. S3) consists of two bands: (i) the additive absorption spectrum of **ADDDS** due to ICT around 365 nm and (ii) a broad band in the visible region around

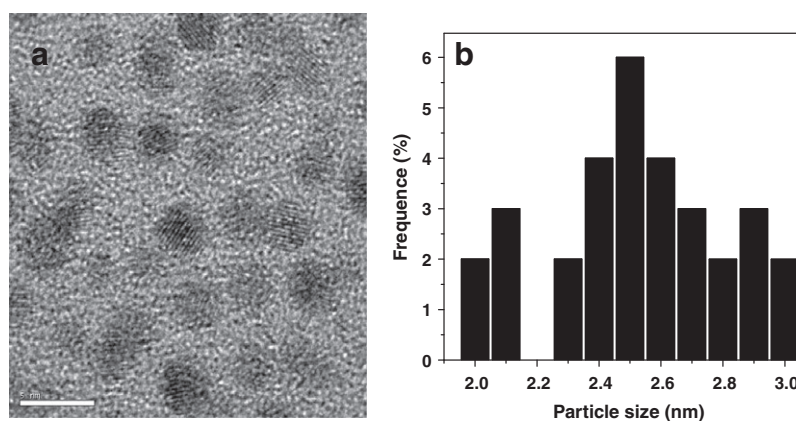


Figure 1. Typical HR-TEM image of **ADDDT-GNP**. (a) The size label is 5 nm. (b) Size-dependent histogram of **ADDDT-GNP**.

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