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Chiral supramolecular gold-cysteine nanoparticles: Chiroptical and nonlinear optical properties☆

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ABSTRACT

Cysteine is a sulfur-containing amino acid that easily coordinates to soft metal ions and grafts to noble metal surfaces. We report a simple synthetic approach for the production of chiral gold-cysteine polymeric nanoparticles soluble in water. Conjugation of cysteine with gold in a polymeric way, leading to ~50 nm diameter nanoparticles, resulted in the generation of new characteristic circular dichroism (CD) signals in the region of 250–400 nm, whereas no CD signal changes were found with cysteine alone. We also investigate their nonlinear optical properties after two-photon absorption. Two-photon emission spectra and first hyperpolarizabilities, as obtained by the hyper-Rayleigh scattering technique, of these particles are presented.

1. Introduction

The chemistry of the sulfur-gold bond [1] is extremely rich and leads to hybrid materials. Such materials encompass gold thiolate coordination oligomers, for instance, $[Au(I)(SR)]_n$ where SR stands for a chemical group containing a sulfur atom [2] and atomically well-defined clusters $[Au_nSR_m]$ [3], to thiols monolayer protected gold nanoparticles(NPs) or supramolecular assemblies like Au(I)(SR) NPs [4] and at the macroscopic level, to flat surfaces. The valence state of gold atoms is expected indeed to have a significant influence on material properties based on gold nanoparticles. While, the majority of gold atoms in nanoparticles are in the Au(0) state under strong reducing conditions, gold atoms in supramolecular assemblies like Au(I)(SR) NPs are in the gold(I) state [5]. As a result, in atomically well-defined clusters of the $[Au_nSR_m]$ stoichiometry, a subtle balance between the Au(0) core and the Au(I)–SR shell leads to fascinating material properties and in particular to highly tunable optical properties [6].

Polymeric Au(I) thiolates, with a linear RS-Au-SR motif, are well-known intermediates observed during nanocluster synthesis. Large polymeric Au(I)(SR) NPs with sizes around 100–150 nm are quickly formed after mixing glutathione (GSH)- with Au^{3+} ions [5]. The dissociation of these large polymeric Au(I) thiolates is then a simple route to produce luminescent gold nanoparticles with mixed valence states [5]. On the other hand, large polymeric Au(I) thiolates can lead

to supramolecular nanostructures with diverse morphologies ranging from strings to lamellar structures [7–9]. These structures present UV–visible absorption spectra with the characteristic features of ligand-to-metal (LMCT) and metal-centered charge transfer (MCCT) transitions [10]. Both absorption and emission properties were found to be sensitive to the coordination environment. In particular, the photo-emission from MCCT transitions are proofs of Au(I)–Au(I) aurophilic interactions between Au(I) atoms [10]. The sensitivity of the optical properties to the coordination environment was recently used as a time-resolved method for the in situ monitoring of the self-assembly of Au(I)–thiolate NPs [7].

Besides versatile absorption and emission properties of supramolecular Au(I)(SR) NPs, chiral nanostructures of coinage metals with observable optical activity have been successfully engineered [11]. This was for example achieved by adding a chiral center in thiolated ligands. For instance, SH-containing amino acids and peptides such as cysteine (Cys), homocysteine (HCys) and glutathione (GSH) are good candidates to produce such hybrid materials with strong chiroptical properties [12,13]. Circular dichroism methods can thus be used for probing L-cysteine in biological fluids on the basis of chiral nanoparticle [14]. Chirality may also play a critical role for enhancing nonlinear optical properties and thus can be of particular importance for 2 photon biosensing and bioimaging, such as circular dichroism second harmonic generation [15]. Nonlinear chiroptical effects of precisely designed chiral plasmonic nanomaterials can be much stronger than such effects

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observed in the linear regime [16,17]. For atomically well-defined Au_nSR_m clusters, the substitution of achiral by chiral ligands was demonstrated as an efficient strategy to induce significant second-order NLO effects to otherwise centrosymmetric clusters [18,19]. To our knowledge, there is no report available on the nonlinear optical properties (NLO) of large supramolecular NPs like Au(I)(SR) NPs. We hereby report a simple synthetic route to produce such supramolecular polymeric NPs with L- and D-cysteine as the thiolated ligand. Chiroptical and nonlinear optical properties, i.e. two-photon emission spectra and first hyperpolarizabilities of these particles are presented.

2. Experimental and methods

2.1. Materials

All the chemicals were commercially available and used as received. Tetrachloroauric(III) acid trihydrate ($HAuCl_4 \cdot 3H_2O$) was purchased from Acros Organics, L- and D-cysteine and racemic DL-cysteine (L- and D-Cys, and DL-Cys), triethylamine (TEA) and glacial acetic acid, methanol (MeOH), diethyl ether (Et_2O) were purchased from Sigma-Aldrich. Ultrapure water with specific resistivity of 18.2 MΩ was used throughout the synthesis.

2.2. Size characterization

Hydrodynamic particle diameters were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS. A 633 nm wavelength laser beam was sent to an infinitely diluted sample maintained at 25 °C and the scattered signal intensity was analyzed at a 173° angle. DLS allowed access to the particle average sizes and the broadness of the size distribution indicated by the poly value. The higher this poly value, the broader the size distribution is. The cumulant analysis method was used.

2.3. X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were carried out using a PHI Quantera SXM instrument (Physical Electronics, Chanhassen, USA) equipped with a 180° hemispherical electron energy analyzer and a monochromatized Al Kα (1486.6 eV) source operated at 15 kV and 4 mA. The analysis spot had a diameter of 200 μm and the detection angle relative to the substrate surface was 45°.

2.4. UV–visible, fluorescence and circular dichroism measurements

UV–vis spectra in solution were recorded using an AvaSpec-2048 fiber optic spectrometer and an AvaLight-DH-S deuterium-halogen light source. Fluorescence excitation and emission spectra were obtained using a Fluoromax-4 Horiba fluorimeter. CD spectra were recorded using a home-made setup based on Photo Elastic Modulator and lock-in amplifier detection devices previously described in Ref. [20].

2.5. Nonlinear optical measurements

The set-up for hyper-Rayleigh scattering (HRS) and two-photon emission (TPE) has been described in details in previous works [21–23]. Briefly, the light source for the HRS and TPE measurements was a mode-locked femtosecond Ti: sapphire laser delivering at the fundamental wavelength of 780 nm and 950 nm pulses with a duration of about 140 fs at a repetition rate of 80 MHz. After passing through a low-pass filter to remove any unwanted harmonic light generated prior to the cell, the fundamental beam of about 300 mW was focused by a low numerical aperture microscope objective into a 0.5 cm spectrophotometric cell containing the aqueous solutions. The HRS and two-photon emission fluorescence (TPEF) light were collected at an angle of

90° from the incident direction by a 2.5 cm focal length lens. The HRS light was separated from the excitation light by a high-pass filter and a monochromator set at the second harmonic wavelength. The HRS light was then detected with a photomultiplier tube working in the single photon counting regime. For the TPE signal, the wavelength of the spectrometer (iHR320 spectrometer) was scanned between 350 nm and 750 nm but the same detection unit was used.

2.6. Computational

Structural and optical properties of gold-cysteinate complexes have been explored theoretically using density functional theory (DFT) and time dependent DFT (TDDFT) calculations as implemented in Gaussian09 [24]. For geometry optimizations the B97D functional [25] including dispersion corrections was used together with Ahlrichs def2-SVP basis set and the appropriate scalar relativistic effective core potential [26]. For the calculation of excited states, the hybrid long-range corrected functional ωB97X-D was used [27]. Oligomers of Au-Cys were optimized using the PM7 semi-empirical Hamiltonian implemented in the MOPAC2012 code [28].

3. Results and discussion

3.1. Synthesis

Au-Cys complexes (L-, D- and racemic) were directly prepared in a 25 ml centrifuge tube. Briefly, 0.38 mmol of cysteine (D- or L-) is dissolved in 20 ml of water and 0.5 ml of triethylamine. 0.5 ml of gold salt (0.127 mmol, 50 mg) is quickly added and the solution is stirred 30 s by inversion (the color becomes slightly yellow). Quickly, 1 ml of glacial acetic acid is added to induce precipitation of Au-Cys which is centrifuged (5 mn/6000 rpm). The supernatant is removed and Au-Cys is redispersed in water (2 ml with 100 μl of TEA, vortex time 5 mn). 20 ml of methanol is then added to precipitate Au-Cys with centrifugation (10 mn/6000 rpm). Au-Cys was also redispersed in 2 ml of water with 10 μl of TEA and precipitated with MeOH (10 ml)/Et_2O(10 ml). After centrifugation (10 mn/6000 rpm), the product is dried in air. For the experiment, the resulting powder is dissolved in water containing 0.1% v/v of TEA.

3.2. Characterization of gold-cysteine NPs

The as-prepared gold-L-cysteine NPs were found to be stable at room temperature for several weeks. The straightforward protocol produced a pure nanomaterial without the need for size separation and achieves large yields (Fig. 1a). A yellow, non-luminescent powder was obtained in this case. The product could be dried and fully redispersed in water with no loss of material or change in chemical identity. Fig. 1b shows the size distributions of the gold-L-cysteine NPs in aqueous solutions obtained by DLS. Only one component with a mean hydrodynamic diameter (HD) of 50 ± 11 nm was observed. Quantitative XPS measurements indicated an Au: Cys ratio close to a 1:1 stoichiometry in gold-cysteine NPs (see Table S1 and Fig. S1). We also used XPS to investigate the valence state of the gold atoms in the NPs. XPS spectra of 20 nm colloidal Au(0) NPs standard and polymeric GS-Au(I) thiolates were obtained showing that the Au 4f7/2 binding energies (BE) are 83.8 and 85.0 eV, respectively [5]. As shown in Fig. 1c, Au 4f7/2 binding energy (BE) of the gold-L-cysteine NPs is 84.8 eV, which is close to that of Au(I) (BE 85.0 eV) in polymeric GS-Au(I) NPs, suggesting the existence of Au(I) in our NPs. Similar results were obtained for D-CysNPs (data not shown).

3.3. Linear optical and chiroptical properties

Because of the strong complexation ability of sulfur-containing cysteine anions (RS-) toward Au(I), the interaction of Ag(I) with Cys