



NIR laser induced TPA enhancement of Zn(II)-terpyridine capped gold nanoparticles for targeting mitochondria



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ABSTRACT

Gold nanostructures have recently received increasing interest in bioimaging application. Herein, a novel nanostructure material was designed by the terminal sulfur of the S ((E)-3-(4-([2,2':6',2''-terpyridin]-4'-yl)styryl)-9-hexyl-9H-carbazole Zn(SCN)₂ complex) modified with Nano gold. It could be used to target mitochondria under two-photon laser confocal microscopy, due to the energy of laser irradiation gained from the absorbed photons to be dispersed as excess heat to the neighboring particles and thus to induce their fusion, compared with free complex. Furthermore, small size Nano-Au composite was synthesized with longer lifetime, larger two photon absorption cross section (σ) and third order nonlinear optical susceptibility ($\chi^{(3)}$) in the near-infrared region (NIR), due to the laser irradiation induced charge transfer from complex to the gold nanoparticles, which attracting potential applications *in vitro* and *in vivo* cellular imaging.

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1. Introduction

Over past decades, the interactions between organic chromophore and metal nanoparticles (NPs) have attracted considerable attention of the scientists who deal with problems of the organic-metal nanohybrids and endeavor to improve their overall application performance [1–6]. Au NPs could be utilized to enhance the optical responses of nearby chromophores, including localized surface plasma resonance (LSPR) [7–9], extremely large extinction coefficients, enhanced second-harmonic generation (SHG) and two-photon photoluminescence (TPPL) [10–14], surface-enhanced Raman scattering (SERS) [15,16] and metal-enhanced fluorescence (MEF) [17,18]. In addition to the aforementioned optical properties, Au also has a variety of inherent attributes that make its nanostructures an attractive platform for biomedical applications [19–21]. In TPPL, the electron is excited by two photons of half the energy relative to the photon in single photon fluorescence (SPPL) and longer excitation wavelength could greatly reducing the level of phototoxicity. Some nonlinear optical materials (NLOM) modified by Au particles resulting in better electronic structure, fine optical properties and good biocompatibility, could apply to the bioimaging.

Mitochondria targeting has been reported over past few decades [22–26]. It is essential organelles that are required for cellular energy production and involved in many other cellular activities, such as lipid modification, maintenance of redox balance, maintenance of calcium balance, and controlled cell death [27,28]. Fluorescence imaging with subcellular resolution offers a unique approach for visualizing morphological details in tissue or cell that cannot be resolved by other medical imaging techniques [29]. As we all known, Mitochondria is polarized as the negative electric potential differences across the inner membranes. In contrast, depolarization, *i.e.* loss of the electric potential, is an indicator of mitochondrial dysfunction. The general trend of mitochondrial depolarization has a close association with cellular apoptosis and thus, is a pathological feature for some major diseases, *e.g.* Parkinson's disease and Alzheimer's disease [30,31]. Therefore, this nano gold modified complex particles targeting mitochondria may cause by the surface excess of Au³⁺.

Our previous work [32] formed a composite material of teryridyl conjugated with nano silver *via* coordination interaction, but the one-photon fluorescence quenching phenomenon and lifetime attenuation make it cannot be better applied to bioimaging. In this work, "fine particles" Au was chose to replace silver nanoparticles simultaneously with the LSPR properties, nonreactivity and bioinert [33]. Despite its extraordinary inertness under most conditions, Au is well-known for its ability to form a relatively strong gold-thiolate (Au–S) bond with compounds containing the thiol

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(-SH) or disulfide group (S-S) [34]. Herein, as continue our previous work, a D- π -A type terpyridyl ligand is chose to coordinate to Zn(SCN)₂, then the two sulfur-terminal metal complex was presented, and Nano gold is used to modified the NLO through the traditional method for Au particles. Fortunately, a novel Au-complex composite material has been obtained with longer lifetime, two-photon absorption (TPA) coefficient (β), TPA cross section (σ), nonlinear refractive index (γ) and third order nonlinear optical susceptibility ($\chi^{(3)}$) than the original complex. This material can be effectively penetrated into cellular mitochondria with phenomenon in two-photon fluorescence microscopy towards HepG2 cells *in vitro*.

2. Experimental sections

2.1. Apparatus

All chemicals were purchased as reagent grade and used without further purification. The solvents were dried and distilled according to standard procedures. IR spectra (4000–400 cm⁻¹), in KBr pressed pellets, were recorded on a Nicolet FT-IR 170 SX spectrophotometer. ¹H NMR spectra were performed on a Bruker 500 Hz Ultrashield spectrometer and reported as parts per million (ppm) from TMS (δ). Coupling constants *J* are given in Hertz. UV–vis absorption spectra were measured on a UV-265 spectrophotometer. The fluorescence spectra in solution were performed with an F-4500 fluorescence spectrophotometer. The concentration of sample solution was 1.0×10^{-5} M. The morphologies were obtained on transmission electron microscope (TEM, JEM-2100). The Raman spectra were recorded with a Labram-HR spectrometer using the 325 nm line of an Ar ion laser for excitation. Fluorescence lifetime measurements were carried out using an HORIBA FluoroMax-4P fluorescence spectrometer equipped with a time-correlated single-photon counting (TCSPC) card. NLO properties were measured by a femtosecond laser pulse and Ti: 95 sapphire system (680–1080 nm, 80 MHz, 140 fs, Chameleon II) as the light source, and all measurements were carried out at room temperature. Zeta Potentials were measured by using a zeta sizer ((Nano ZS90, Malvern Instruments, UK)) at a temperature of 25 °C.

2.2. Synthesis of nanostructure material S–Au NPs

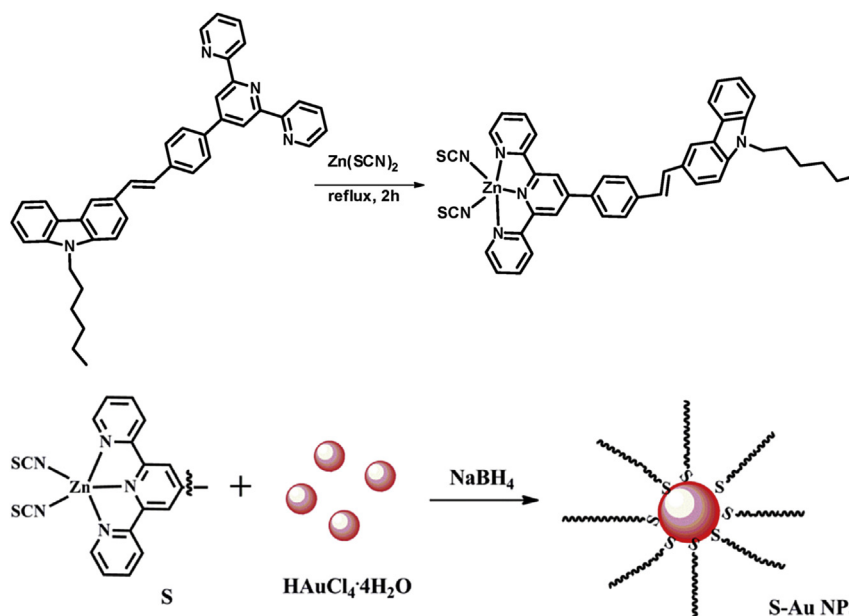
Synthesis of complex (named **S** blow) is accorded to our reported method [35], which is in Scheme 1. The ligand has been published [32]. ¹H NMR (DMSO-*d*₆, 400 MHz): (ppm) = 0.81–0.84 (m, 3H), 1.21–1.30 (m, 6H), 1.80 (m, 2H), 4.43 (m, 2H), 7.75 (m, 1H), 7.42–7.51 (m, 3H), 7.63–7.72 (m, 3H), 7.82–7.84 (d, 1H), 7.92–7.98 (m, 4H), 8.19–8.21 (d, 1H), 8.35–8.49 (m, 5H), 8.86 (s, 1H), 9.09–9.16 (m, 3H), 9.44 (s, 1H). *m/z* (%): 762.369 (M⁺). (Fig. S1).

According to an article [36], HAuCl₄·4H₂O (3.3 mL, 0.08 mmol) and polyvinyl pyrrolidone (PVP) (0.094 mmol, 0.01 g) were firstly put in the round bottom flask. Then, 25 mL DMF solution of **S** (0.24 mmol) was added dropwise to the above solution with magnetic stirring at ice-water bath for 1 h. At this stage, the Au(III) combine with **S** to form a transparent orange S–Au³⁺ sol. Then, a freshly prepared 7 mL DMF solution of NaBH₄ (0.015 g) was fleetly injected into the sol and instantly generated an orange fluid. Stirring was continued for overnight at low temperature and the nanoparticles powder was obtained by subsequent centrifugation of the precipitate, followed by washing several times with a distilled water-DMF mixture and vacuum drying. Finally the dark brown S–Au composite nanoparticles (NPs) were got.

3. Results and discussion

3.1. Characterization of S–Au NPs

TEM image of S–Au NPs with particle sizes of 5 nm was shown in Fig. 1. From the image, the surface of the Au particles was obviously capped with **S**. FT-IR of S–Au NPs was shown in Fig. 2. The peak 2167 cm⁻¹, identified as characteristic peak of SCN⁻, blue shifts to 2085 cm⁻¹ after the formation of complex **S**, then blue shifts to 2078 cm⁻¹ and the intensity reduces when capped with Au particle. Moreover, in Fig 3 the Raman spectra of **S** and S–Au NPs, the peaks 1174.3 cm⁻¹, 1190.3 cm⁻¹ identified as out-of-plane ring bend of pyridine were shifted at 1179.1 cm⁻¹, 1195.6 cm⁻¹, respectively, indicating that the terpyridyl moiety actually interacted with Au nanoparticles to some extent.



Scheme 1. Synthesis of S–Au NPs.

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