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Ground and excited state behavior of 1,4-dimethoxy-3-methyl-anthracene-9,10-dione in silver nanoparticles: Spectral and computational investigations

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ABSTRACT

Silver nanoparticles (Ag NPs) of various sizes have been successfully synthesized by the simple and convenient Creighton method using sodium borohydride as the reducing agent under microwave irradiation. Optical absorption and fluorescence emission spectroscopic techniques were employed to investigate the effect of silver nanoparticles on the ground and excited state of 1,4-dimethoxy-3-methylanthracene-9,10-dione (DMMAD). The surface plasmon resonance (SPR) peak of the prepared silver colloidal solution was observed at 400 nm. Fluorescence quenching of DMMAD by silver nanoparticles has been found to increase with increase in the size of Ag. The fluorescence quenching has been explained by Forster Resonance Energy Transfer (FRET) theory between DMMAD and silver nanoparticles. The Stern–Volmer quenching constant and Benesi–Hildebrand association constant for the above system were calculated. DFT calculations were also performed to study the charge distribution of DMMAD in Ag both in ground and excited states.

1. Introduction

Anthraquinone, also called as anthracenedione or dioxoanthracene, is an aromatic organic compound. It is the most important quinone derivative of anthracene [1]. Anthraquinones are widely applied in medicine, food, paper, pharmaceutical chemistry and dye industry. In the pharmaceutical industry, the natural and synthetic derivatives of anthraquinone are beneficial to mammals and humans as they can display antibacterial, antitrypanosomal and antineoplastic activities [2]. It is used in wood preservatives, insecticides, organic light emitting diodes and coating materials. Anthracene derivatives have been the subject of extensive research mainly due to their well-recognized biological importance and the significant biological applications [3].

Nanotechnology, inextricably a multidisciplinary field, has an explosive growth in the past decade due to its extremely hefty applications in various fields of nanoscale electronics, optics, magnetics, energy, catalysis, nanomedicines, clothing, cosmetics, etc. [4]. Among all nanostructured materials, Ag NPs have attracted considerable interest from the chemical industry and medicine due to unique properties, such as high thermal conductivity, high resistance of oxidation, and antibacterial activity [5–9].

NP synthesized from silver has created great interest, because of their surface plasmon resonance (SPR). Ag is one of the most frequently used metals for fluorescence enhancement because of its low cost. The noble metal NP's are used in photography, catalysis, biological labeling, photonics, biosensors, drug delivery in cancerous tumors, optoelectronics, information storage, surface enhanced Raman scattering (SERS), formulation of magnetic ferrofluids, cosmetic and beauty applications [10].

Fluorescence is one of the most leading technology commonly used in life sciences because of its versatility and wide spread potential applications in the areas of luminescence tagging, imaging, medical, diagnostics, multiplexing and most recently in biosensors [11].

Fluorescence quenching refers to any process that decreases the fluorescence intensity of a sample. A variety of molecular interaction can result in quenching. It includes excited-state reactions, molecular rearrangements, energy transfer, ground-state complex formation, and collisional quenching. Fluorescence quenching is studied both as a fundamental phenomenon, and as a source of information about the biochemical systems. Quenching studies can be used to reveal the localization of fluorophores in proteins and membranes, and their permeabilities to quenchers.

Investigation of metal NPs like Ag and Au has increased interest in the interactions of fluorophores with metallic surfaces or particles. The intensity of fluorophores near Ag particles is usually increased, and fluorophores near Au particles are usually quenched [12]. The interactions of fluorophores with metal nanoparticles results in the

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fluorescence enhancement, increased photostability, decreased lifetime because of increased rates of system radiative decay and increased transfer distances for FRET [13].

In particular the NPs have promising applications as bright fluorescent markers with enhanced photostability in fluorescence microscopy, sensor technology, and microarrays. The enhancement or quenching of the fluorescence emission of molecules near a metal surface arises from interactions with surface plasmon resonance (SPR) in the metal particles. These interactions may also result in shortening of the excited-state lifetime thus improving the photostability of the dye. The optical properties of a fluorescent molecule located near the metal nanoparticles are affected by the near-field electro dynamical environment [14]. This can cause an enhancement or quenching of the fluorescence depending on the distance between the molecule and the metal surface. In the case of fluorescent molecules located at very short distances from a metal surface, non-radiative energy transfer to surface plasmon in the metal takes place [15].

Our group has studied the fluorescence quenching of anthraquinone derivatives in Ag NPs environment [16,17]. In the present study, optical absorption and fluorescence emission spectroscopic techniques have been employed to investigate the effect of Ag NPs on the ground and excited state of 1,4-dimethoxy-3-methylanthracene-9,10-dione (DMMAD) (Fig. 1).

2. Experimental

2.1. Materials

Silver nitrate ($AgNO_3$, 99.5%) and sodium borohydride ($NaBH_4$, 95%) were purchased from MERCK. Spectral grade methanol (C_2H_5OH) was purchased from NICE. 1,4-dimethoxy-3-methyl anthracene-9,10-dione (DMMAD) were synthesized according to the literature [18]. All the chemicals were of analytical grade and used as purchased without further purification.Double distilled water was used throughout the experiment.

2.2. Preparation of Ag NPs using Creighton method

Ag NPs used in this study were synthesized by the Creighton method [19]. In brief, silver nitrate solution (0.6 mM) and sodium borohydride solution (1.2 mM) were individually prepared in distilled water with vigorous stirring (1 h). Both the solutions were kept separately in ice cooled temperature. 8 ml of ice cooled silver nitrate solution is added drop wise to 25 ml of sodium borohydride solution (S1). It was repeated for different volumes of silver nitrate solution (12, 16 and 20 ml) (S2, S3 and S4) at constant volume of sodium borohydride (25 ml). The prepared solution was golden yellow in color. The prepared colloidal Ag NPs solution was heated in microwave oven for 60 s. During the preparation in a microwave oven, the golden yellow solution turned to the characteristic yellowish brown color, then to grayish black, indicating the formation of Ag NPs.

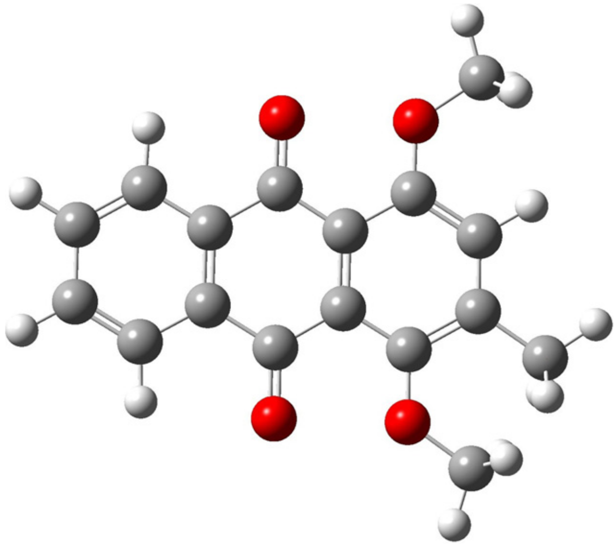

Fig. 1. Structure of 1,4-dimethoxy-3-methylanthracene-9,10-dione (DMMAD).

The concentration of DMMAD in methanol was 0.02 mM. To investigate the effect of Ag NPs on DMMAD, the above solution and silver sol were mixed in 1:1 volume ratio.

2.3. Apparatus

Optical absorption spectra were recorded using a Shimadzu UV-1700 pharmaspec UV–visible spectrophotometer. Jobin Yvon Flurolog-3-11 Spectrofluorometer was used to record the emission spectra. The excitation wavelength is 450 nm.

2.4. Fluorescence quantum yield

Parker's method was employed to determine the relative fluorescence quantum yield (ϕ_{rel}) in which 1,4-dihydroxy-2,3-dimethyl-9,10-anthraquinone (DHDMAQ) was used as fluorescence standard ($\phi = 1.0836 \times 10^{-3}$) [20]. In the present case, the fluorescence quantum yield of DMMAD in methanol was found to be 5.4134.

3. Result and discussion

3.1. Computational Studies

The structure and electronic properties of the ground and excited states for DMMAD and DMMAD+Ag have been simulated. The optimization of DMMAD and DMMAD+Ag is carried out using Gaussian 03 software. Density functional theory (DFT) is useful to evaluate a variety of ground state properties. Ground state geometries are performed with DFT, LSDA with 3–21 G basis set. Configuration interaction singles (CIS) excited states calculations are performed to get excited state configurations. LANL2MB is a double zeta basis set contains effective core potential representations of electrons near the nuclei for post-third row atoms. LANL2MB basis set is used for CIS calculations.

The charge distribution (Mullikan) and dipole moment vector in both ground and excited states for DMMAD and DMMAD+Ag systems are shown in Fig. 2. The dipole moment of DMMAD in the ground state is 2.7445 Debye. In the excited state, the dipole moment is 3.0812 Debye. In the excited state charge of the whole system is increased. When silver atom is added into DMMAD, the dipole moment of DMMAD+Ag system is 5.6005 Debye. In the excited state the dipole moment of the system is 8.3940 Debye. The observed optimized geometry shows that the DMMAD can interact with Ag NP through C$=$O group of DMMAD, which makes DMMAD adsorbed in stand-on orientation which leads to higher dipole moment.

3.2. Optical properties of silver nanoparticles

UV–vis absorption spectra of prepared Ag NPs at different volume ratios are shown in Fig. 3. Table 1 shows the observed surface plasmon resonance peak and full width at half maximum (FWHM) values of the prepared silver nanoparticles. The maximum absorption