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Understanding fluorescence resonance energy transfer between biologically active coumarin derivative and silver nanoparticles using steady state and time resolved spectroscopic methods

V.V. Koppal [a], R.M. Melavanki [b], R.A. Kusanur [c], N.R. Patil [a,*]

[a] Department of Physics, B V B College of Engineering and Technology, Hubli 580031, Karnataka, India
[b] Department of Physics, M S Ramaiah Institute of Technology, Bangalore 560054, Karnataka, India
[c] Department of Chemistry, R.V. College of Engineering, Bangalore 560059, Karnataka, India

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ABSTRACT

This work confines the study of fluorescence resonance energy transfer (FRET) of biologically active fluorescent probe 3ADHC to silver nanoparticles (*AgNPs*) at room temperature. Steady state and transient state spectroscopic measurements have been employed to get the insight on fluorescence quenching mechanism. Stern-Volmer plots for steady state and transient state are found to be linear and it is attributed to collisional quenching mechanism. Steady state and transient state quenching constants are correlated and an efficient fluorescence quenching was observed. The influence of concentration of *AgNPs* on the absorption of 3ADHC molecule is analyzed by Benesi–Hildebrand equation. Quantum yield (ϕ) of the 3ADHC molecule was estimated by relative method as 0.582. The distance between acceptor-donor (r_0) is found to be less than 70 Å. In accordance with FRET theory there is a significant energy transfer between 3ADHC molecule and *AgNPs*.

1. Introduction

Resonance energy transfer is an electro-dynamic phenomenon in which the transfer of energy takes place from an excited donor fluorophore to a proximal ground-state acceptor fluorophore within a relative distance between them. It's extremely sensitive to distance between acceptor and donor within nanometre scale and their relative dipole orientations. Resonant energy transfer systems consisting of fluorophore-fluorophore or fluorophore- nanoparticles have gained considerable interest in the field of analytical chemistry, protein conformation studies, biological assays and bio-photonics etc. [1].

Numerous qualitative and quantitative studies on FRET have shown that, the luminescence properties of the fluorescent probes can be significantly altered by near-field interactions produced by the metallic nanoparticles. The nature, shape and size of the metallic nanoparticles can greatly trigger the fluorescence of a targeted fluorescent probe within an optimal distance. Due to electronic coupling between the acceptor and donor dipole moments results in enhancement of fluorescence efficiency. Recently, the studies on FRET have described that "FRET in association with the recent advancement in optical techniques" provide a way to understand the biological systems at the molecular level [2], "Growing applications for bioassembled Förster resonance energy transfer cascades" provided a perspective on unique combination of photonically active biomaterials may transition to concerted applications [3]. In addition to it, FRET has multidimensional applications such as Specific cell imaging [4], Ultra small silver nano-clusters as energy acceptors [5], multiplexing [6], luminescence tagging [7] and biolabeling [8] etc.

Coumarin is a naturally available organic compound found in many plants. Coumarins have excellent charge transfer properties which are used as precursor reagent in many pharmaceutical industries to synthesis a number of synthetic anticoagulant drugs [9]. Coumarins are the prime members of benzo α pyrones which belong to a category of benzopyrones in which benzene is fused with a pyrone ring. The substitution pattern of the coumarins can influence the pharmacological, therapeutic and biochemical applications [10]. Fluorescence quenching studies of biologically active 4 aryloxymethyl coumarin dyes with TiO_2 NPs reveals static quenching mechanism, electron transfer process and the role of binding between them [11]. The role of silver nanoparticles on spectroscopic properties on substituted coumarin derivatives reveals the presence of both static and dynamic quenching mechanisms [12]. Steady state and transient state studies of pharmacologically active phenothiazine derivative with TiO_2 NPs reveals the dynamic quenching mechanism and the role energy transfer between them [11,13].

Studies have confirmed that coumarins serve as antioxidants [14], anticancer [15], anti-neoplastic [16], antimicrobial [17,18], antineuro degenerative [19], chemosensors [20], anticoagulants [21,22] etc.,

* Corresponding author.
E-mail address: patilnr23@gmail.com (N.R. Patil).

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Among various organic molecules, coumarin based donor-acceptor (D-A) model charge-transfer complexes and compounds are considered to be very promising materials in the field of molecular electronics for the development of the molecular scale systems such as molecular wires, molecular optoelectronic triggering switches, molecular transistors and molecular memories etc. [23].

From the ongoing literature survey, no FRET study has been undertaken so far on this title molecule and hence it has triggered us to understand the resonance energy transfer of (3ADHC) with *AgNPs*. With the help of different quenching models, Stern-Volmer constant and various other quenching rate parameters have been determined. Therefore, our study signifies that, there is an efficient transfer of energy between the *AgNPs* and 3ADHC molecule.

2. Experimental

2.1. Materials

Coumarin derivative 3ADHC was synthesized by our group [24,25]. The molecular structure of 3ADHC is presented in Fig. 1. Analytical grade silver nitrate and starch were purchased from S-D Fine Chemicals Ltd., India. The HPLC grade solvent acetonitrile (ACN) and deionised water were purchased from S-D-Fine Chemicals Ltd., India and are used as received without further purification. All the glassware were cleaned in chromic acid and rinsed with deionised water and dried in the hot air oven prior to use. The required quantity of solution of 3ADHC in ACN solvent was prepared at a fixed solute concentration of 1×10^{-6} M.

2.2. Synthesis of silver nanoparticles (AgNPs) and size determination

Silver nanoparticles (*AgNPs*) of uniform size were synthesized by microwave assisted process as suggested in the reference [26]. Using the transmission electron microscopy (TEM) the size of the synthesized *AgNPs* was determined. The absorption surface plasmon resonance peak of *AgNPs* is observed at 420 nm and is shown in Fig. 2. The TEM image of the synthesized silver nanoparticles is shown in Fig. 3. The average size of the *AgNPs* is found to be 12 nm.

2.3. Steady state measurements

Absorption spectra of the 3ADHC and synthesized *AgNPs* were recorded in absorption spectrophotometer (Model: Hitachi U-3300 UV/VIS, Maryland, United States) at room temperature. The fluorescence spectra of 3ADHC in different concentrations of AgNPs were recorded using Spectrofluorometer (Model: Hitachi F-7000 Spectrofluorometer, Tokyo, Japan) with perpendicular geometry. All the glassware were washed in deionised water and dried in electric oven prior to use.

2.4. Time resolved fluorescence measurements

The fluorescence lifetime (τ) was recorded on TCSPC nanosecond fluorescence lifetime spectrometer based on Time Correlated Single Photon Counting technique (Model: ChronosBH ISS 90021). This setup has lifetime measurement ranging from 10^{-12}–10^{-2} s. Consists of Laser diode with excitation wavelength 405 nm as excitation source. The detector system composed of photomultiplier tube (PMT) which operates in the wavelength ranging from 185 to 850 nm. While recording lifetime of 3ADHC the emission wavelength is set at 475 nm. The minimum time channel width of this setup is 820 fs and it has total useful count rate up to 4 MHz. The lifetimes of fluorescence decay profile of 3ADHC molecule in ACN solvent without and with quencher are recorded at room temperature. The lifetime of 3ADHC in ACN solvent is single exponential with $\tau_0 = 0.297$ ns. Generally the average lifetime is calculated using the equation $\tau_0 = (\tau_1 a_1 + \tau_2 a_2)/100$, where τ_1, τ_2 are the lifetimes and a_1, a_2 are the corresponding amplitudes.

All the experimental results are reproducible within 5% of the experimental uncertainties.

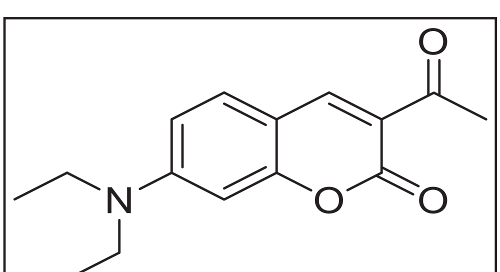

Fig. 1. The molecular structure of 3ADHC molecule.

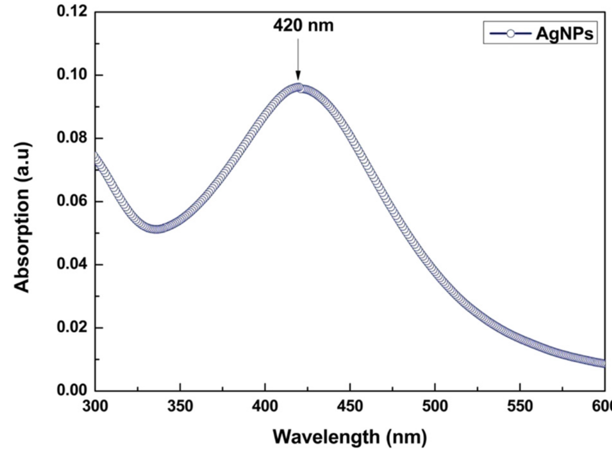

Fig. 2. Typical absorption spectrum of AgNPs at room temperature.

3. Results and discussion

3.1. Effect of AgNPs on absorption characteristics of 3ADHC

The absorption spectrum of synthesized *AgNPs* in ACN solvent was recorded at room temperature and is given in Fig. 2. It displays the typical surface plasmon resonance peak at 420 nm. Fig. 4 shows the typical absorption spectra of 3ADHC molecule in different concentrations of *AgNPs* (0.00 mM to 0.10 mM) in ACN solvent at room temperature. From the Fig. 4 it is observed that as the concentration of AgNPs

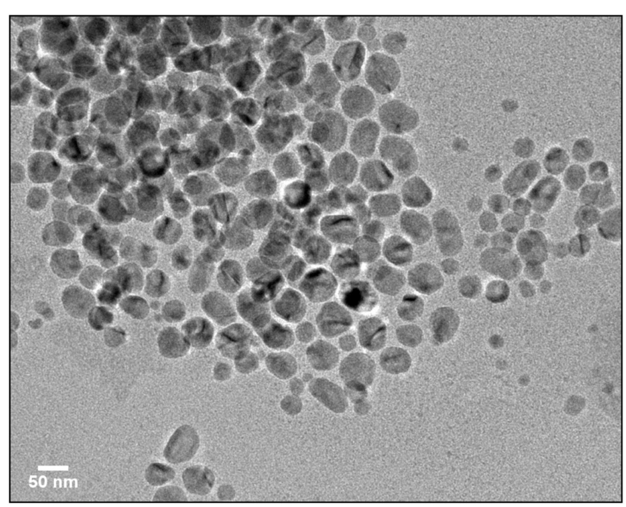

Fig. 3. TEM image of the AgNPs using microwave irradiation method.