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Quenching of Fluorescent ADS680HO molecule with Eco-Friendly Synthesized Silver Nanoparticles

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ABSTRACT

In this work, we have collected spectroscopic optical fluorescence and absorption spectra of the highly fluorescent laser dye molecule ADS680HO in different spectroscopic grade solvents with and without the amalgamation of eco-friendly synthesized silver nanoparticles (AgNP's), which resulted in the spectral intensities displaying quenching in the fluorescence and absorption intensities. It attributes the shape, dimension and bonding between the AgNP's and ADS680HO molecules, as well as the transfer of energy among the fluorescent probe and AgNP's. Fluorescence quenching of dye has innumerable uses for progress in cutting-edge bio-molecular labeling, fluorescence patterning and cancer treatment with chemotherapy.

Keywords: *SPR, RET, ADS680HO, absorption, fluorescence, quenching, AgNP's*

1. Introduction

This research paper explains a thorough understanding of the extremely fluorescent dye ADS680HO ($C_{37}H_{39}N_2O_6Cl$) of per chlorate series [1–7]. Spectroscopic studies of this molecule have sparked the curiosity to take the task in thorough understanding of the molecule. This aids to develop and tailor new types of molecules that can be used for specific applications, like [3] dye lasers, lithography, biosensors, microbiological schemes, dye based printing methods, molecular equipment, chemotherapy in the treatment of fatal diseases like cancer, extensive use in energy transformation phenomena, labeling proteins in bio-medical chemistry, to have comprehensive knowledge of fluorescence quenching., etc. By assuming extensive applications as an industrially important ADS680HO dye molecule, a complete understanding of its photo physical and behavioral nature inspires a complete, systematic report in this task.

In this communication, we report the quench of optical fluorescence along with the absorption spectra of ADS680HO dye molecule by naturally synthesized AgNP's. The quenching property of ADS680HO has immense industrial and medical applications, like chemotherapy to treat cancer. However, till now, no perfect and systematic study has been conducted by any investigator to explain the effects of absorption and fluorescence of this compound. Hence, it is our opportunity to disclose new exclusive, unique optical studies on fluorescence quenching with optical absorption studies of ADS680HO molecules and eco-friendly AgNP's.

Spectroscopic fluorescence and absorption spectra related to ADS680HO fluorescent molecules without and with AgNP's in different solvents are documented on the UV-VIS Spectra Suite Spectrometer with complete software (high-resolution model HR-4000 model, having resolution ±0.1nm). Various graphs are plotted on Origin software.

2. Investigation Section

2.1 Spectroscopic Measurements

Spectroscopic fluorescence and absorption spectra related to ADS680HO fluorescent molecules without and with AgNP's in different solvents are documented on the UV-VIS Spectra Suite Spectrometer with complete software (high-resolution model HR-4000 model, with resolution ± 0.1nm). Various graphs are plotted on Origin software.

2.2 Materials Used

American laser fluorescent ADS680HO dye was procured at ADS Source, Inc., and its structural and molecular formula is depicted in Fig. 1. Solvents are the alcohol series, acetonitrile, DMSO, ethyleacetate, toluene, glycerol, and benzene. Solvents are purchased from Sigma Aldrich and are of spectroscopic grade. Concentrations of the solution could be in the range of 10^{-5} mol/L. $AgNO_3$ salt is obtained from Himedia Laboratories Pvt. Ltd., India. All solution preparations are carried out using ultra-deionized water.

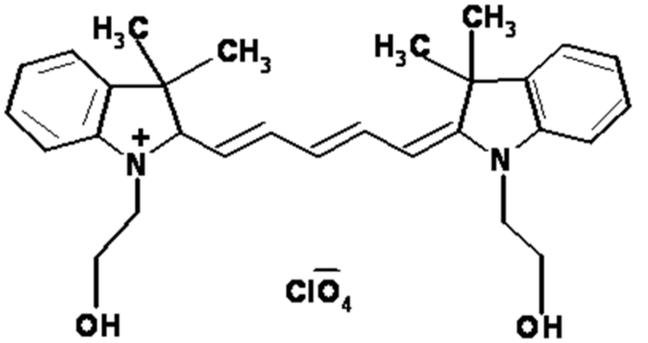

Fig. 1: Molecular Structure and IUPAC name of ADS680HO.

Molecular formula : $C_{37}H_{39}N_2O_6Cl$ (commercial name ADS680HO)

IUPAC Name : 2-[5 -(1, 3-Dihydro-3, 3-dimethyl- (2- hydroxyethyl)-2H-benzindol-2-ylidene) -1, 3-pentadienyl]-3, 3-dimethyl-1-(2-hydroxyethyl)-3Hbenz[e] indolium perchlorate.

2.3 Green Nanotechnology: Preparation of Silver Nanoparticles (AgNP's) by Krishna Tulasi leaves

Fresh Krishna Tulasi (Ocimum Sanctum) plant leaves are washed thoroughly using deionized water. 40g of Ocimum sanctum leaves were thoroughly washed and boiled in 100 ml of distilled water to prepare the extraction. Further, the extract was filtered and stored at 40 °C for future experimental work. This extract is used to reduce and stabilize the synthesis of

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silver nanoparticles. 1.5 ml of extract to 20 ml of silver nitrate ($AgNO_3$) (concentration of silver nitrate is 2 mM) solution on a magnetic stirrer container. The color turns yellow within 5–6 minutes. This color-changing property is an indication of the formation of silver nanoparticles. Here, Krishna Tulasi extract is composed of certain phytochemicals, namely: urosolic acid, euginal, eugenol,linalool, carvacrol, limatrol, caryophyllene, sitosterol, anthocyans methyl, and caricol. These phytochemicals are mainly responsible for the reduction of $AgNO_3$ salt to AgNP's. This chemical reduction reaction was carried out on a magnetic stirrer based hot plate at room temperature.

3. Surface Plasmon Resonance (SPR) of Eco-friendly synthesized silver nanoparticles

Nanoparticles have been specifically examined through Mie's scattering theory using Maxwell's electromagnetic equations regarding their dependence on the size of the particle and the surrounding medium. Mie's theory [8–13] is a Maxwell's electromagnetic explanation with mathematical calculations of the scattering of electromagnetic radiation by spherical nanoparticles. According to Mie's scattering theory, the particular size of the nanoparticles exposed by the particular wavelength results in a peak resonant wavelength. Two separate approaches based on particle size and target probe range can explain this. The first strategy is, limit of 2R << λ, (R is the radius of the nanoparticle and λ is the wavelength of incident electromagnetic radiation), where the electric dipole term oscillates maximum under the influence of exposed electromagnetic radiation, which is expressed expressively [8] as extinction cross-section (σ_{ext}), i.e., an explanation of the surface plasmon resonance (SPR) spectrum. Optical absorption spectrum is taken in the range of 325-575 nm region.

$$C_{ext} = \frac{24\pi R^3 \varepsilon_m^{\frac{3}{2}}}{\lambda} \frac{\varepsilon''}{(\varepsilon'+2\varepsilon_m)^2+\varepsilon''} \quad (1)$$

ε′ real and ε′′imaginary portions in the complex dielectric function $\varepsilon_m \left(\varepsilon_m = \varepsilon' + i\varepsilon''\right)$.

Second strategy is based on condition to SPR which is according to Maxwell's equation.

$$\varepsilon' = -2\,\varepsilon m \quad (2)$$

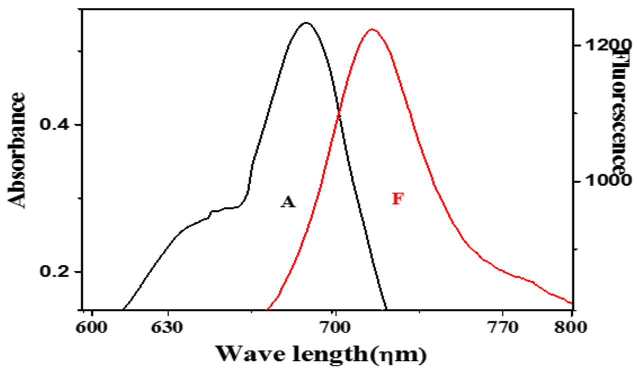
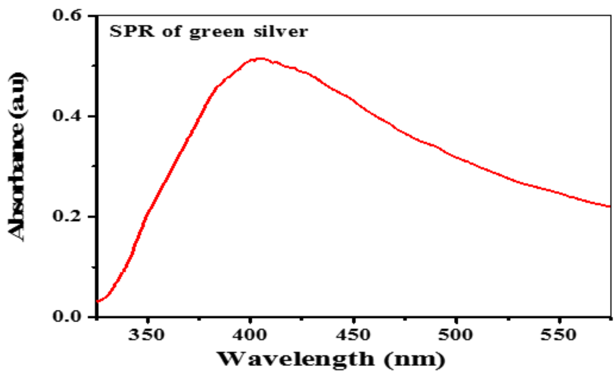


Fig. 2: Optical absorption and fluorescence spectra of ADS680HO in decanol solvent



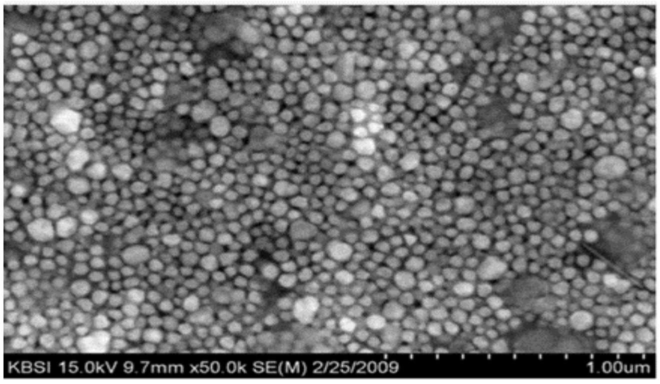


Fig. 3: SPR absorption spectra of eco-friendly synthesized nanoparticles of Silver. SEM (Scanning Electron Microscope) image.

In case of small AgNP's, dipole moment is experienced by an incident electric field which promotes the formation of surface polarization, i.e., charge, which predominantly affects the regaining of force by free electrons. The bottom line is that a higher wavelength of bulk metal absorption maintains a smaller surface plasmon band, thus, satisfying the equation-2.

4. Optical Fluorescence and Absorption Intensities Quenching of ADS680HO Laser Dye

This investigation reveals that fluorescence and absorption quenching were experientially noticed for ADS680HO laser dye in various alcohol solvents attached to AgNP's through hydrogen bonding. The emission and absorption spectra of ADS680HO before the influence of silver nanoparticles are shown in Fig. 2.

Typically, quenching in intensities of absorption and fluorescence is mainly attributed to energy rate transfer from probemolecules to AgNP's which is governed by [14] the following three factors [14]:

1. SPR band width
2. Peak position
3. Coulumbic interaction

Columbic interactions on energy transfer are due to the following two reasons:

1. Interaction among probe molecules with AgNP's it is subjected to densities of the charges.
2. Interaction between dipoles within the medium.

Charge density and dipole moment of a dye with AgNP's are related to energy transfer among dye molecules from the silver particle, which explains quenching of optical absorption in the ultra-violet region. This shows a band around 670–700 nm (ADS680HO), and is assigned π-π* transitions. This amalgamation of AgNP's and the chosen target dye molecule encourages strong quenching or enhancement [9–19] of fluorescence intensities, which is appreciably observed conditionally depending upon the nature and physical conditions of the target molecule.

Widening SPR describes the variety of molecules that are near AgNP's and the absorption / fluorescence intensity that may quench or enhance them. The width of the curve depends on the nature of the attaching molecules and is a function of the bonding between probe molecules and AgNP's. In our case, absorption and fluorescence quenching are noticed because of the close distance between AgNP's and ADS680HO. If fluorescent dye directly bonds to nanoparticles, it definitely reveals that fluorescence is completely and heavily quenched. Hence, in the present discussion, attachment is a little longer in range i.e bond length is larger, so intensity in quenching is rather low.

The size of nanoparticles affects the presence of the precise band of SPR in various alcoholic targeted solvents in conjugation with ADS680HO molecules was Examine Through the ultra-violet absorption spectrum at the range 300-600 nm Fig. 3. A series of alcohols are selected to definite reactions with alcoholic groups (–OH), nitrile, and chlorate groups in ADS680HO dye, which primes the patent properties of the silver and gold nanoparticle optical properties. If nanoparticle size becomes appreciably greater than the wavelength of the excitation (λ>> 2R), energy transfer can be estimated and confirmed with minor and extended regions of SPR. Silver nanoparticles and their spectroscopic properties are greatly prejudiced by respective their dimension, shapes, and nearby environmental conditions. The final thing to say is that resonant plasmon energy transfer is among tightly spaced nanoparticles, and the surrounding environment also matters.

The RET (Resonance Energy Transfer) model [9-19] was created on nonradiative decay, providing complete theoretic and thoughtful observations of quenching fluorescence behavior. These specific light interaction properties of metallic and dielectric molecules specifically investigated experimentally and also theoretically, are of prime interest in the current trend. If a particle is excited and oscillates with SPR in the presence of an incident electro-magnetic wavelength spectrum region, the excited system has an appreciably disturbing effect and a change in dipole moment, which shows the radiation response. Particularly, this optical radiation from dipole moments delivers a channel for the process of radiative decay. Instead, the Joule effect and surface plasmon absorption may cause non-radiative decay. The struggle between radiative and non-radiative decay energy transfer greatly affects the fluorescence emission spectra of the molecules located near the particles. Suppose non-radiative decay takes the major ruling effect, and fluorescence quenching phenomena happens. So, the variable distance behavior of the radiative and non-radiative rates explains quantum yield declines at a short distance from metal nanoparticles [5, 19-21].

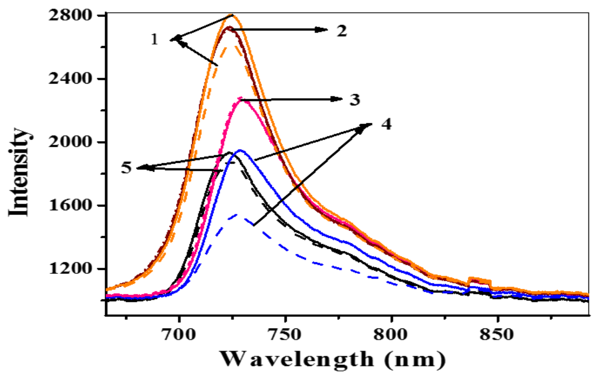


Fig. 4: Optical absorption spectra of Silver nanoparticles with (dotted)/ without (lined) in conjugation with ADS680HO along with solvents (1- methanol, 2-ethanol, 3-propanol, 4-butanol, 5-octanol).

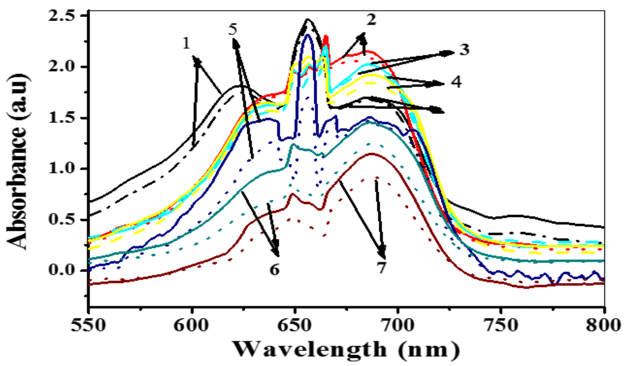


Fig. 5: Fluorescence image of silver nanoparticle with (dotted)/ without (lined) in conjugation with ADS680HO along with solvents (1-methanol, 2-ethanol, 3-octanol, 4-butanol, 5-ethanol, 6-decanol, 7-nonanol).

Our particular experimental quenching of fluorescence Fig. 4 is credited to RET from laser dye ADS680HO to eco-friendly synthesized nanoparticles. Particularly, this special non-radiative decay is assigned to the studies of the theory of Forster resonance energy transfer (FRET) [5, 22, 23]. A small amount of AgNP's is injected into ADS680HO dye solution in different alcohol solvents. Target dye molecules have a very high affinity to form complex clusters that surrounding's, which causes physical adsorption and results in optical quenching intensity. At higher concentrations of ADS680HO, large number of molecules adsorb on the AgNP's, improving the effectiveness of quenching. This quantum efficiency yield of AgNP's is given by FRET theory as below. Here Q is the quenching efficiency of quantum yield [5].

$$Q = \frac{\Gamma^R}{\Gamma^R + \Gamma^{NR}} \quad (3)$$

Γ^{NR}– non-radiative decay and Γ^R – radiative decay;

Presently, attachment of AgNP's to ADS680HO dye results in larger non-radiative decay and leads to quantum efficiency declination, Hence, it leads to fluorescence quenching. Fig. 4 and 5. Here, quenching is static and could also be attributed to an attachment of the dye with silver nanoparticles via complexes of the nanometal with –OH, nitrile, and chlorate groups Fig. 6.

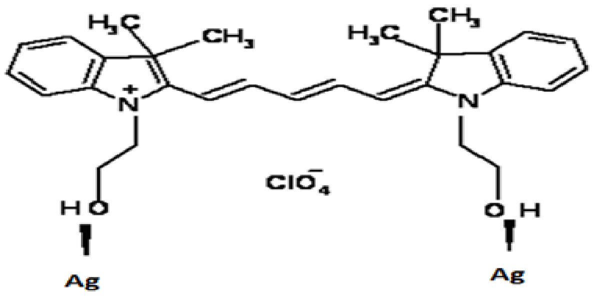


Fig. 6: Conjugation of AgNP's withADS680HO molecule.

5. Conclusions

Spectroscopic optical fluorescence and absorption spectra of ADS680HO molecule in various alcohol complexes with and without AgNP's show spectral intensities quenching. This is due to the probe's molecular dimension, its shape, coupling between the AgNP's and energy transfer between them. The intensity quenching property of fluorescence using AgNP's with ADS680HO leads to numerous and advanced usages, particularly fluorescence patterning, advanced in bio-molecular labelling, cancer chemotherapy treatment and many more.

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