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# Study of Role of Silver Nanoparticles on Spectroscopic Properties of a Ketocyanine Dye

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## Abstract

The role of silver nanoparticles on spectroscopic properties of the ketocyanine dye 2,5-di[(E)-1-(4-dimethylaminophenyl) methyldine]-1-cyclopentanone (2,5-DMAPMC) has been investigated using absorption and fluorescence spectroscopy. Silver nanoparticles are synthesized by chemical reduction method and estimated size from SEM measurements is 22 nm. The changes in absorption spectrum of dye in the presence of silver nanoparticles suggest the possible interaction with silver nanoparticles. The Stern-Volmer plot of fluorescence quenching is found to be nonlinear showing positive deviation. The magnitude of quenching rate parameter and fluorescence lifetime measurements indicates the presence of both collisional and static quenching mechanisms. The binding constant and number of binding sites for static part of the quenching have been

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estimated from the fluorescence data. The role of diffusion and electron transfer processes in fluorescence quenching mechanism has been discussed.

**Keywords:** Ketocyanine dye, Silver nanoparticles, Quenching, Binding site, Electron transfer

## 1. Introduction

Ketocyanine dyes are one of the important class of dyes which exhibit excellent solvatochromic behavior. These dyes are reported to be promising probes for monitoring micro-polarity, metal ion sensing, hydrogen-bond donating interaction, investigation of the cell membrane structures, evaluating the micro-environmental characteristics of biochemical and biological systems and many more [1-6]. A ketocyanine dye 2,5-di[(E)-1-(4-dimethylaminophenyl) methylidene] -1- cyclopentanone(2, 5-DMAPMC) is also reported to be exhibiting such interesting properties. Even though thorough investigations have been carried out with respect to photophysics and photochemistry of 2,5-DMAPMC, there is a dearth of information on the interaction of this dye with nanoparticles in general and silver nanoparticles in particular.

The investigations on interaction of dyes with nanoparticles has attracted significant attention due to the fact that integration of nanotechnology with biology and medicine is expected to produce major advances in molecular diagnostics, therapeutics and bioengineering [7,8]. Among the metal nanomaterials, silver nanoparticles have received considerable attention due to their good antibacterial, antifungal and antiseptic properties. It has been reported that silver nanoparticles in the size regime 1-10 nm bind to HIV-1 virus and prevent it from bonding to host biological cells [9]. Excellent probe nature of 2,5-DMAPMC, and potential applications of dye-nanoparticle systems, motivated us to carry out the present work.

In continuation of our investigation on spectroscopic properties of fluorescent organic molecules and because of the importance of study of interaction of fluorescent molecules with silver

nanoparticles, the present investigation is carried out. The aim of the present work is to systemically study the role of silver nanoparticles on absorption and fluorescence properties of 2,5-DMAPMC. Experimental data is analysed by using Benesi-Hildebrand model, Stern-Volmer (S-V) equation and Rehm-Weller equation for electron transfer.

## 2. Material and Methods

### 2.1. Materials

Ketocyanine dye 2,5-DMAPMC was synthesized in our lab and its structure is confirmed by NMR. The molecular structure of dye is shown in Figure 1. Methanol used in the present study is of spectroscopic grade and is obtained from S.D. Fine Chemicals Ltd., India. Analytical grade silver nitrate ( $\text{AgNO}_3$ ) and sodium borohydride ( $\text{NaBH}_4$ ) were also obtained from S.D. Fine Chemicals, India. Double distilled water was used in the preparation of aqueous solutions.

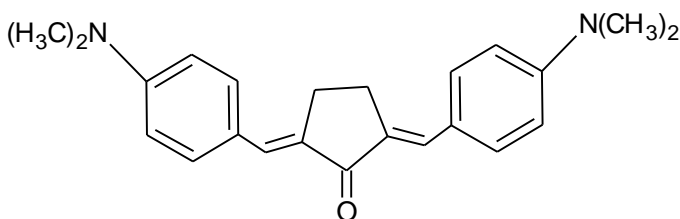


Fig 1. Molecular structure of 2,5-DMAPMC

### 2.2. Absorption, fluorescence and lifetime measurements

The absorption and fluorescence spectra were recorded in methanol in the presence of silver nanoparticles by using UV-VIS spectrophotometer (Model: Shimadzu UV-1800) and fluorescence spectrophotometer (Model: Hitachi F-2700) respectively at room temperature. In order to reduce the self-absorption effects, measurements were carried out at low concentration of dye ( $2 \times 10^{-5}$  M).

Fluorescence lifetime measurements were carried out using a picosecond time correlated single photon counting (TCSPC-Model:

chronosBH, Make: ISSINCUSA) spectrometer. This set up has lifetime measurement range of  $10^{-11}$ s to  $10^{-2}$ s. The excitation source used is a light emitting diode with excitation wavelength of 480 nm. The detector system comprises of photomultiplier tube (PMT) which operates in the wavelength range 185nm - 850nm. The emission wavelength is at 607 nm. The minimum time channel width of this setup is 820 fs and it has total useful count rate up to 4 MHz. The observed fluorescence decay curves were analyzed using a reconvolution program, which is an iterative nonlinear least squares fit method. The goodness of fit was evaluated by  $\chi^2$  criterion and visual inspection of residuals of the fitted function to the data. In the present case the decay profile was bi-exponential.

### 2.3. Synthesis and estimation of size of silver nanoparticles

Silver nanoparticles were synthesized by chemical reduction method which involves the reduction of silver nitrate solution by sodium borohydride solution. The details of synthesis were reported in our previous work [10]. In this method, sodium borohydride and silver nitrate were used in 6:1 ratio for better stability of silver nanoparticles as suggested by Solomon [11].

The size of silver nanoparticles was estimated by employing Scanning Electron Microscope (SEM) using CARL ZEISS ULTRA-55 FESEM under high vacuum mode. For the preparation of substrate for SEM, the sample holder was covered with double sided carbon tape and a small quantity of silver nanoparticles was added to the carbon tape. This was degassed for 24 hours in vacuum desiccator. The SEM image of silver nanoparticles is shown in Figure. 2. The SEM image indicates the presence of spherical nanoparticles with few other shapes as well. The average size of silver nanoparticles is found to be 22 nm.

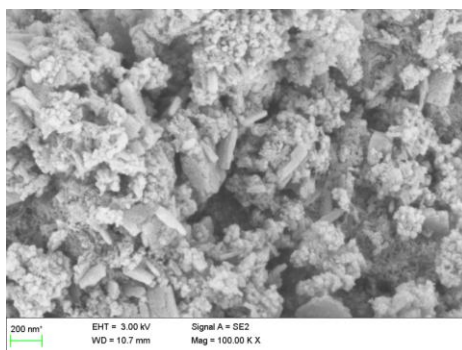


Fig 2.SEM image of silver nanoparticles.

## 2.4. Cyclic voltametric measurements

The oxidation potential of 2,5-DMAPMC in methanol was measured by cyclic voltametry experiment on the AUTOLAB electrochemical device using a cell equipped with three electrodes, the working electrode (Pt disc), the counter electrode (Pt disc) and the reference electrode (Saturated Calomel Electrode (SCE)). The cyclic voltammograms were recorded at a scan rate of  $100 \text{ mV S}^{-1}$ .

## 3. Results and Discussion

### 3.1. Role of silver nanoparticles on absorption characteristics of 2,5-DMAPMC

The optical absorption spectrum of synthesized silver nanoparticles in water shows a surface plasmon resonance peak at  $388 \text{ nm}$ (Fig.3).

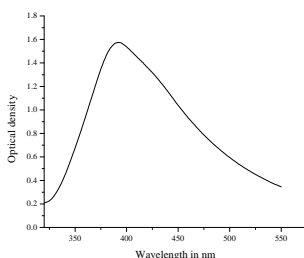


Fig3.Absorption spectrum of silver nanoparticles.

The optical absorption spectrum of dye 2,5-DMAPMC in methanol was recorded in the absence and presence of silver nanoparticles. The concentration of silver nanoparticles was varied from 0 to  $31.72 \mu\text{M}$  with respect to the analytical concentration of silver. The

absorption spectrum of 2,5-DMAPMC in the absence and presence of silver nanoparticles is shown in Figure 4.

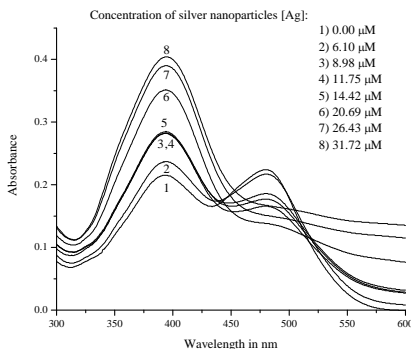


Fig 4. Absorption spectra of 2,5-DMAPMC in the absence and presence of silver nanoparticles.

The increase in optical density at the absorption maximum of dye and broadening of spectra is observed in the presence of silver nanoparticles. Also, the absorption maximum of dye is slightly blue shifted with the addition of silver nanoparticles. These changes in absorption spectrum indicate the possible interaction between 2,5-DMAPMC and silver nanoparticles. The changes in intensity of absorption peak as a result of formation of surface complex can be used to obtain association constant ( $k_a$ ) of dye with silver nanoparticles in the ground state according to Benesi-Hildebrand equation as given below [12].

$$\frac{C}{\Delta A} = \frac{1}{\Delta \varepsilon_a} + \frac{1}{\Delta \varepsilon_a k_a [Ag]} \quad (1)$$

Where  $C$  is the concentration of dye,  $\Delta A$  is the change in absorbance of dye with and without silver nanoparticles at its  $\lambda_{\max}$ ,  $\Delta \varepsilon_a$  is the change in absorption coefficient and  $[Ag]$  is the analytical concentration of silver. The plot of  $\frac{C}{\Delta A}$  versus  $\frac{1}{[Ag]}$  according to equation (1) is found to be linear and is shown in Figure 5.

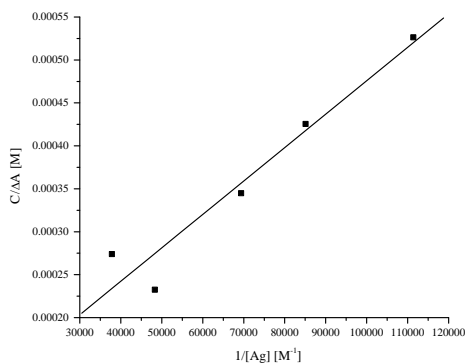


Fig 5. Plot of  $C/\Delta A$  versus  $1/[Ag]$  for 2,5-DMAPMC.

From the slope and intercept of this plot,  $k_a$  value is found to be  $2.22 \times 10^4 M^{-1}$ . The value of  $k_a$  is within the range of those previously reported for other dyes [10, 13-15]. This indicates the strong association between silver nanoparticles and the dye investigated.

### 3.2. Influence of silver nanoparticles on fluorescence characteristics of 2,5-DMAPMC

The steady state fluorescence spectrum of 2,5-DMAPMC in methanol is recorded in the absence and presence of silver nanoparticles. The fluorescence spectrum of 2,5-DMAPMC in the absence and presence of silver nanoparticles is shown in Figure 6.

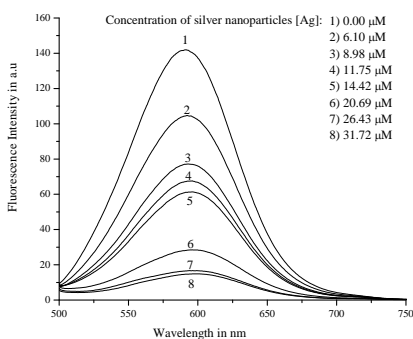


Fig 6. Fluorescence spectra of 2,5-DMAPMC in the absence and presence of silver nanoparticles.

From, Figure. 6, it is noticed that as the concentration of silver nanoparticles increases, the shape of fluorescence band does not change but there is a red shift of 8 nm as the concentration of silver nanoparticles is increased from 0 to 31.72  $\mu\text{M}$ . Also, there is an appreciable quenching of fluorescence intensity of the dye with increase in the concentration of silver nanoparticles. To understand the quenching of fluorescence intensity, Stern-Volmer (SV) plot is drawn as shown in Figure 7 according to the following equation [16]:

$$\frac{I_0}{I} = 1 + K_{SV} [Ag] \quad (2)$$

where  $I_0$  and  $I$  are fluorescence intensities of dye respectively in the absence and presence of silver nanoparticles and  $K_{SV}$  is Stern-Volmer quenching constant. From Figure 7, it is clear that SV plot of fluorescence quenching is non-linear showing positive deviation. The value of  $K_{SV}$  was determined from the lower portion of SV plot and is found to be  $3.37 \times 10^4 \text{ M}^{-1}$ . The quenching rate parameter  $k_q (= K_{SV} / \tau_0)$  is found to be  $1.07 \times 10^{15} \text{ M}^{-1}\text{s}^{-1}$  where  $\tau_0$  is

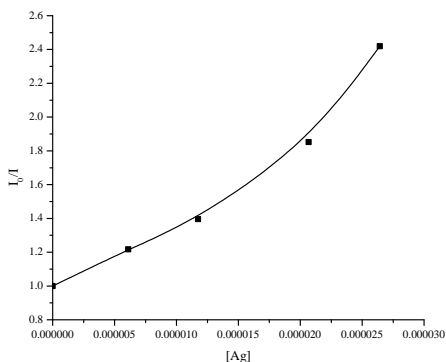


Fig 7. SV plot for 2,5-DMAPMC.

the fluorescence lifetime of 2,5-DMAPMC in the absence of silver nanoparticles (0.0315 ns). It is well known that the value of maximum collisional  $k_q$  for various quenchers to bio molecules is of the order of  $10^{10} \text{ M}^{-1}\text{s}^{-1}$  [16]. But, in the present case, higher quenching rate parameter of the order of  $10^{15} \text{ M}^{-1}\text{s}^{-1}$  was obtained. This shows that quenching of 2,5-DMAPMC by silver nanoparticles



could be due to static quenching, which arises because of the formation of complex between the dye and silver nanoparticles. In order to find out whether quenching is purely static, fluorescence lifetime ( $\tau$ ) measurements were carried out. The typical fluorescence decay profile in the absence and presence of silver nanoparticles is shown in Figure 8. The fluorescence decay curves of 2,5-DMAPMC with and without silver nanoparticles are double exponential according to

$$I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$$

where the subscripts 1 and 2 refer to the shorter and longer pre-exponential components respectively of the decay and,  $a_1$  and  $a_2$  are the corresponding relative amplitudes. The lifetime values were obtained by fitting experimental decay profiles to double exponential function (using reconvolution procedure) to get  $\chi^2$  values very close to unity. From Figure 8, it is clear that fluorescence lifetime of 2,5-DMAPMC did not change with increase in the concentration of silver nanoparticles (overlapping of decay profiles). Therefore, positive deviation in SV plot is mainly due to static quenching process [16].

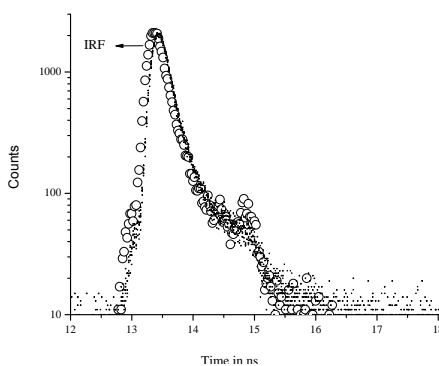


Fig 8. Fluorescence decay profile of 2,5-DMAPMC in the absence and presence of silver nanoparticles.

### 3.3. Estimation of binding constant and number of binding sites

For the static quenching, if it is assumed that there are independent binding sites to a set of equivalent sites on a macromolecule, the apparent binding constant and the number of binding sites can be determined according to the following equation [17].

$$\log \left[ \frac{I_0 - I}{I} \right] = \log k_b + n \log [Ag] \quad (3)$$

where  $k_b$  is the binding constant of silver nanoparticles with 2,5-DMAPMC, which can be determined from the intercept of the plot of  $\log \left[ \frac{I_0 - I}{I} \right]$  versus  $\log [Ag]$  as shown in Figure 9.

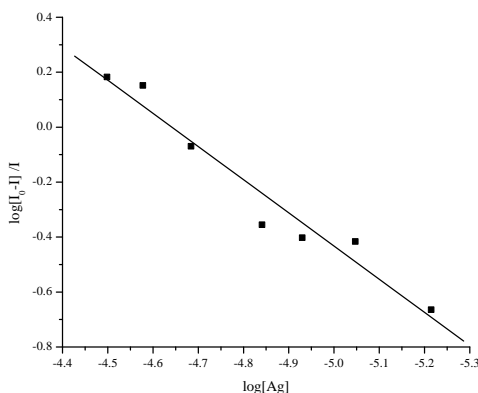


Fig 9. Plot of  $\log \left[ \frac{I_0 - I}{I} \right]$  versus  $\log [Ag]$  for 2,5-DMAPMC.

The calculated value of binding constant ( $k_b$ ) is  $4 \times 10^5 \text{M}^{-1}$  and number of binding sites ( $n$ ) is 1.2. The value of ' $n$ ' implies that there exists only one binding site in 2,5-DMAPMC for silver nanoparticles.

### 3.4. Role of diffusion in fluorescence quenching

To investigate the role of diffusion in fluorescence quenching, the diffusion rate parameter  $k_d$  is estimated using Umberger-Lamer equation [18] as given below.

$$k_d = 4\pi N' DPR \quad (4)$$

where  $N'$  is Avogadro's number per millimole,  $D$  is the sum of diffusion coefficients of dye and silver nanoparticles, and is calculated using Stokes-Einstein relation [19],  $P$  is the probability of quenching per encounter and is taken to be unity, and  $R$  is the sum of molecular radii of dye and silver nanoparticles. The radius of dye molecule was estimated using the method suggested by J.T.

Edward [20]. The value of  $k_d$  calculated using equation (4) is found to be  $14.85 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ , it is clear that value of  $k_d$  is smaller than  $k_q$ . This indicates that the fluorescence quenching of 2,5-DMAPMCby silver nanoparticles is not just controlled by diffusion. This is the expected result for static quenching process.

### 3.5. Role of energy transfer and electron transfer in fluorescence quenching

Since there is no overlap of absorption spectrum of silver nanoparticles with the emission spectrum of 2,5-DMAPMC, the possibility of energy transfer process between silver nanoparticles and 2,5-DMAPMC is ruled out. Hence the study of electron transfer process is taken up in the present investigation. The role of electron transfer in fluorescence quenching of 2,5-DMAPMCby silver nanoparticles is explained by the well-known Rehm-Weller formula [21]. Rehm-Weller formula given by equation (5) is used to understand the thermodynamic feasibility of the excited singlet state electron transfer reaction.

$$\Delta G_{et} = E_{1/2}^{(ox)} - E_{1/2}^{(red)} - E^* + C \quad (5)$$

where  $\Delta G_{et}$  is the free energy change for the electron transfer reaction,  $E_{1/2}^{(ox)}$  is the oxidation potential of 2,5-DMAPMC (0.0029 V as obtained from cyclic voltametry measurements) and  $E_{1/2}^{(red)}$  is the reduction potential of silver nanoparticles. The reduction potential of silver nanoparticles (- 0.09 V) with silver as reference electrode is taken from literature [22]. The reported reduction potential of silver nanoparticles is converted against saturated calomel electrode (SCE) by subtracting 0.3 V from the measured potential [23].  $E^*$  is the excited singlet state energy of 2,5-DMAPMC (2.59 eV) which is calculated using the crossing point of emission and excitation spectra and  $C$  is the coulombic term (0.00245 eV). The  $\Delta G_{et}$  value has been calculated and is found to be -2.20 eV. The higher negative value of  $\Delta G_{et}$  indicates the presence of electron transfer process which is thermodynamically favorable [24, 25]. In order to understand the extent of contribution of electron transfer process in overall quenching mechanism, the rate constant for electron transfer  $k_{et}$  is calculated according to equation (6) in accordance with Marcus theory [26].

$$k_{et} = \nu \exp\left(\frac{-\Delta G^*}{kT}\right) \quad (6)$$

where  $\Delta G^*$  is free energy of activation and is given by

$$\Delta G^* = \frac{(\Delta G_{et} + \lambda)^2}{4 \times \lambda} \quad (7)$$

and  $\nu$  is the frequency factor whose value ranges from  $10^{12}$  to  $10^{14} \text{ s}^{-1}$  depending on the systems [27, 28]. In the present study, maximum value of  $\nu$  ( $=10^{14} \text{ s}^{-1}$ ) is considered for  $k_{et}$  calculation. In equation (8)  $\lambda$  is the total reorganization energy, given by the sum of the internal reorganization energy  $\lambda_{in}$  and solvent reorganization energy  $\lambda_s$ :

$$\lambda = \lambda_{in} + \lambda_s \quad (8)$$

$\lambda_{in}$  has an insignificant contribution, which is an expectable fact in diffusion conditions [29]. In case of electron transfer between organic molecules diffusing freely in solution, the solvent reorganization energy  $\lambda_s$  is considered to be the most important term [30]. The value of  $\lambda_s$  is calculated according to equation (9)

$$\lambda_s = e^2 \left( \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}} \right) \times \left( \frac{1}{\mu^2} - \frac{1}{\epsilon} \right) \quad (9)$$

where  $\mu$  and  $\epsilon$  are refractive index and dielectric constant of solvent (methanol),  $r_A$  is the radius of electron acceptor ( $4.34 \text{ \AA}$  for 2,5-DMAPMC),  $r_D$  is radius of electron donor (silver nanoparticles,  $220 \text{ \AA}$ ) and  $r_{DA}$  is considered to be equal to the sum of  $r_D$  and  $r_A$  values. The value of  $k_{et}$  calculated according to equation (6) is  $3.08 \times 10^5 \text{ s}^{-1}$ . The magnitude of  $k_{et}$  indicates the substantial contribution of electron transfer in overall quenching mechanism.

#### 4. Conclusions

The role of silver nanoparticles on 2,5-DMAPMC has been studied. The absorption spectral changes indicate the possible interaction between the dye and silver nanoparticles. The observed fluorescence quenching of 2,5-DMAPMC by silver nanoparticles is

due to static quenching mechanism. For static quenching the binding constant and the number of binding sites were estimated from fluorescence data. It has been observed that fluorescence quenching is not solely controlled by diffusion. Electron transfer between the dye and silver nanoparticles also plays a role in overall quenching mechanism. To the present day, this is the first study on the role of silver nanoparticles on spectral properties of 2,5-DEAPMC.

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