



# Spectroscopic interactions of titanium dioxide nanoparticles with pharmacologically active 3(2H)-pyridazinone derivative



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## ABSTRACT

Herein, we report the spectroscopic interactions of titanium dioxide (TiO<sub>2</sub>) nanoparticles (NPs) with pharmacologically active 3(2H)-pyridazinone derivative, viz., 5-(2-Hydroxy-4-methyl-phenyl)-2-phenyl-2H-pyridazin-3-one [HMP] in an ethanol solvent using UV–Visible spectrophotometer, fluorescence spectrophotometer and time-correlated single photon counting technique at room temperature. The observed values of absorption, fluorescence intensity and fluorescence lifetime of HMP molecule decrease with increasing in the TiO<sub>2</sub> NPs concentration. From the linear Stern–Volmer (S-V) plot in steady state and transient state which indicates the presence of dynamic quenching. The association constant ( $k_a$ ) and quenching constant ( $K_{SV}$ ) have been estimated using Benesi–Hildebrand and S-V equations respectively. Further, from the fluorescence data we calculated the binding constant and number of binding sites, the results reveals that there exists one binding site in HMP molecule for TiO<sub>2</sub> NPs. In addition, we studied the energy transfer in fluorescence quenching by Forster's non-radiative energy transfer (FRET) theory. Results, signified that the fluorescence quenching of the HMP molecule is due to the energy transfer from HMP molecule to TiO<sub>2</sub> NPs. The present investigation may be adopted in solar energy materials and also exploited in a variety of applications such as biological sensing, medical diagnosis etc.

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## 1. Introduction

The rapid advancement of nanotechnology is most apparent when one can consider the phenomenal growth in the numbers of consumer products that contain nanomaterials. A wide range of nanomaterials types has been used in commercial products, including metal oxides, rare earth oxides and polymers [1–4]. One of the most versatile metal oxide nanoparticles (NPs) is titanium dioxide (TiO<sub>2</sub>) were used in many applications. Recently, the use of TiO<sub>2</sub> NPs in different consumer and medical products such as pharmaceuticals, sunscreen and detergents [5]. Further, they have been applied TiO<sub>2</sub> NPs in the field of photocatalytic degradation [6], dye-sensitized solar cells [7], antibacterial activity [8] and anticancer treatment [9].

The 3(2H)-pyridazinones are the pyridazine derivatives contain two adjacent nitrogen atoms at the 1 and 2 positions in a six-membered ring and a carbonyl group at the 3 position and they have different functionalities in their structure [10–11]. A substantial number of pyridazinones in the recent past have been reported to possess antimicrobial, antitubercular, analgesic, anti-inflammatory, cyclooxygenase inhibitor, antidiabetic, antihypertensive, antiplatelet, anticancer, antifungal,

antidepressant–anxiolytic, anticonvulsant, bronchodilatory (for asthma) and anti-allergic, antifeedant, inhibition of linolenic acid, activity for neurological disorders and many other properties. Some of the major pyridazinone derivatives which have appeared in the market are indolidan, bemoradan, pimobendan, levosimendan as antihypertensive, minaprine as an antidepressant, emorfazone as anti-inflammatory and azanrinone as a cardiotonic [12]. Recently, spectroscopic and quantum chemical investigations on 3(2H)-pyridazinone derivatives such as levosimendan and bromopyrazone compounds have been studied [13–14]. In addition, the detailed structural, conformational, spectroscopic, electronic and nonlinear optical properties of the 3(2H)-pyridazinone derivatives namely flufenpyr (used in agriculture as an herbicide) and amipizone (designed to be antithrombotic and an inhibitor for platelet aggregations and the cardiovascular system) compounds estimated at the B3LYP, B3PW91 and HSEH1PBE levels of theory with the basis set 6-311G (d, p) [15]. Soliman et al. reported the molecular structure, spectroscopic properties, NLO, HOMO–LUMO and NBO analyses of 6-hydroxy-3(2H)-pyridazinone [16]. Recently, we have reported the ground and excited state dipole moments of 3(2H)-pyridazinone derivatives using solvatochromic approaches [17–18].

The phenomenon of fluorescence quenching competes with the spontaneous emission and causes the reduction in the fluorescence intensity and lifetime of the fluorescence molecules. Generally, it is a

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process in which the electronic excitation energy of an excited molecule is transferred to a quencher molecule via several mechanisms such as diffusion, charge transfer etc. and it leads to the non-fluorescent emission of quencher molecule [19]. The fluorescence quenching of organic molecules in solvents by various quenchers like carbon tetrachloride [20], aniline [21–23], oxygen [24], TiO<sub>2</sub> NPs [25], silver NPs [26] and SnO<sub>2</sub> NPs [27] have been a subject of continued investigators for last two decades. The application of quenching phenomenon is very useful in physical science, chemical science and medical science [28–29].

In view of the pharmacological and spectroscopic importance of TiO<sub>2</sub> NPs, 3(2H)-pyridazinone derivatives and fluorescence quenching phenomenon we have prompted to study the spectroscopic properties and the influence of TiO<sub>2</sub> NPs concentration on HMP molecule. In the present case, UV–Visible spectrophotometer, fluorescence spectrophotometer and time-correlated single photon counting techniques have been employed to understand the nature of the fluorescence quenching of HMP molecule.

## 2. Materials and methods

### 2.1. Materials

The 3(2H)-pyridazinone derivative 5-(2-Hydroxy-4-methyl-phenyl)-2-phenyl-2H-pyridazin-3-one [HMP] molecule was synthesized according to reference [30] and its molecular structure is shown in Fig. 1. The solvent ethanol is spectroscopic grade and it was purchased from S.D. Fine Chemicals Ltd., India. Titanium dioxide (TiO<sub>2</sub>) nanoparticles (NPs) were purchased from HiMedia Laboratories Pvt. Ltd. India. Quencher was prepared using TiO<sub>2</sub> NPs in 5 mL of ethanol solvent of  $1 \times 10^{-5}$  M/L concentration. Solutions were prepared to keep the concentration of solute HMP fixed ( $1 \times 10^{-5}$  M/L) and varying TiO<sub>2</sub> NPs concentrations (0.00 μM/L, 0.06 μM/L, 0.13 μM/L, 0.20 μM/L, 0.26 μM/L and 0.33 μM/L).

### 2.2. Spectroscopic measurements

The absorption spectra were recorded using UV–visible spectrophotometer [Model: Hitachi U-3310 at USIC K. U. Dharwad, India] and fluorescence spectra were recorded in absence and presence of the TiO<sub>2</sub> NPs using fluorescence spectrophotometer [Model: Hitachi F-7000 at USIC K. U. Dharwad, India]. The fluorescence lifetimes were recorded in the absence and presence of the TiO<sub>2</sub> NPs using time-correlated single photon counting technique [TCSPC ISS model: 90021 at USIC K. U. Dharwad, India]. All these spectroscopic measurements were carried out at room temperature [300 K]. The experimental values are reproducible within 5% of an experimental error.

### 2.3. Benesi–Hildebrand equation

The change in the absorption value of HMP molecule by adding different concentrations of TiO<sub>2</sub> NPs is analyzed using the Benesi–Hildebrand equation [31] and is given below

$$\frac{C}{\Delta A} = \frac{1}{\Delta \epsilon} + \frac{1}{\Delta \epsilon k_a [\text{TiO}_2]} \quad (1)$$

where  $k_a$  is association constant.  $C$ : Concentration of HMP molecule.  $\Delta A$ : Change in absorbance of HMP molecule with and without TiO<sub>2</sub> NPs at its maximum absorption wavelength.  $\Delta \epsilon$ : Change in absorption coefficient.  $[\text{TiO}_2]$ : Concentration of TiO<sub>2</sub> NPs.

### 2.4. Stern–Volmer [S-V] equation

The change in the fluorescence intensity and fluorescence lifetime of HMP molecule by adding different concentrations of TiO<sub>2</sub> NPs is analyzed using the S-V equation [19] and is given below

For steady state

$$\frac{F_0}{F} = 1 + K_{sv} [\text{TiO}_2] \quad (2)$$

For transient state

$$\frac{\tau_0}{\tau} = 1 + K'_{sv} [\text{TiO}_2] \quad (3)$$

where  $F_0$  and  $F$  are the fluorescence intensities in the absence and presence of quencher respectively.  $\tau_0$  and  $\tau$  are the fluorescence lifetimes in the absence and presence of quencher respectively,  $[\text{TiO}_2]$  is quencher concentration.  $K_{sv} = k_q \tau_0$  ( $K'_{sv} = k'_q \tau_0$ ) is the S-V constant, which is obtained from the slope of S-V plot and  $k_q$  ( $k'_q$ ) is quenching rate parameter.

### 2.5. Binding constant formula

The relationship between fluorescence intensity of HMP molecule and concentration of TiO<sub>2</sub> NPs can be described by the binding constant formula [32] and is given below

$$\log \frac{F_0 - F}{F} = \log k_b + n \log [\text{TiO}_2] \quad (4)$$

where  $k_b$  is the binding constant,  $n$  is the number of binding sites.

### 2.6. Energy transfer in fluorescence quenching

The energy transfer in fluorescence quenching of HMP molecule by TiO<sub>2</sub> NPs is studied using the Forster's non-radiative energy transfer theory (FRET) [19], in this the energy transfer takes place between donor (HMP molecule) and acceptor (TiO<sub>2</sub> NPs) when the following conditions are obeyed

- 1) The donor emits fluorescence.
- 2) The emission spectrum of the donor and the absorption spectrum of acceptor must be overlap.
- 3) The distance between donor and acceptor is less than 70 Å.

The energy transfer efficiency ( $E$ ) between donor and acceptor can be obtained by following Eq. (5)

$$E = 1 - \frac{F}{F_0} \quad (5)$$

where  $F_0$  and  $F$  are the fluorescence intensity of donor in the absence and presence of acceptor respectively.

The value of critical energy transfer distance ( $R_0$ ) (when the energy transfer efficiency is 50%) is given below

$$R_0 = 0.211 \left[ k^2 \Phi n^{-4} J \right]^{1/6} \quad (6)$$

where  $k^2 = 2/3$  is the orientation factor relating the geometry of the donor-acceptor dipoles,  $n$  is the refractive index of ethanol solvent,  $\phi$

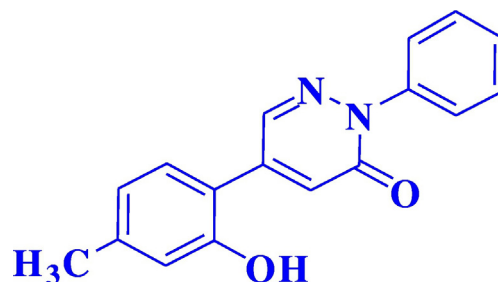


Fig. 1. The molecular structure of HMP molecule.

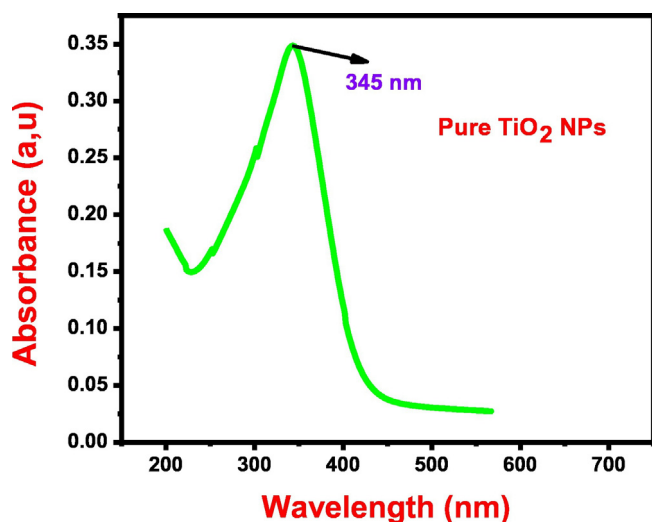


Fig. 2. The absorption spectrum of TiO<sub>2</sub> NPs in ethanol solvent.

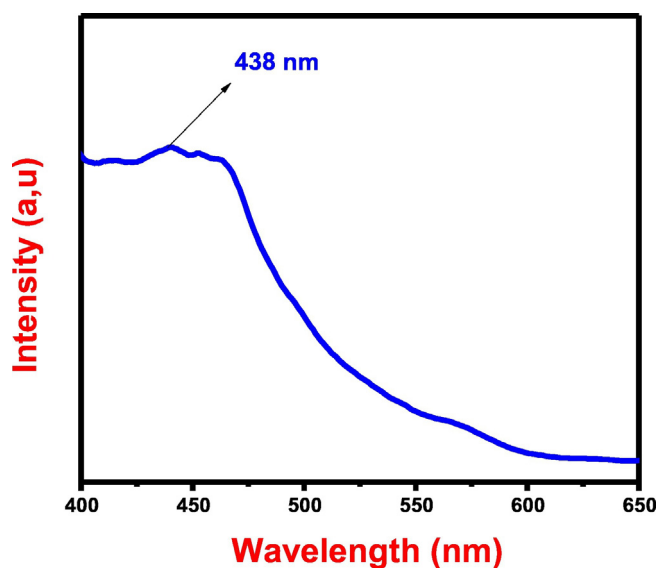


Fig. 3. The emission spectrum of TiO<sub>2</sub> NPs in ethanol solvent.

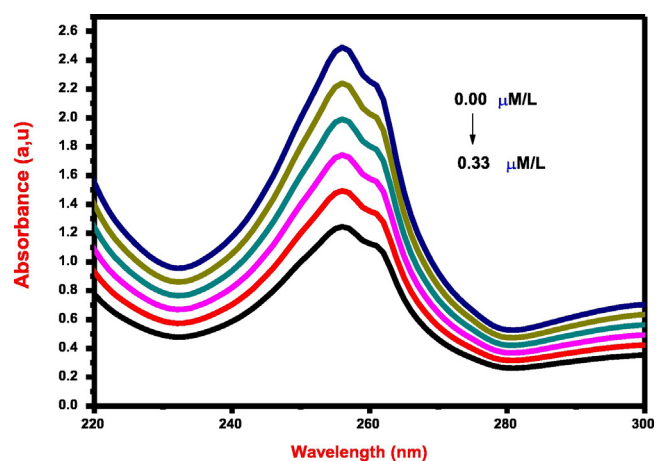


Fig. 4. The absorption spectra of HMP molecule in ethanol solvent for different concentrations of TiO<sub>2</sub> NPs.

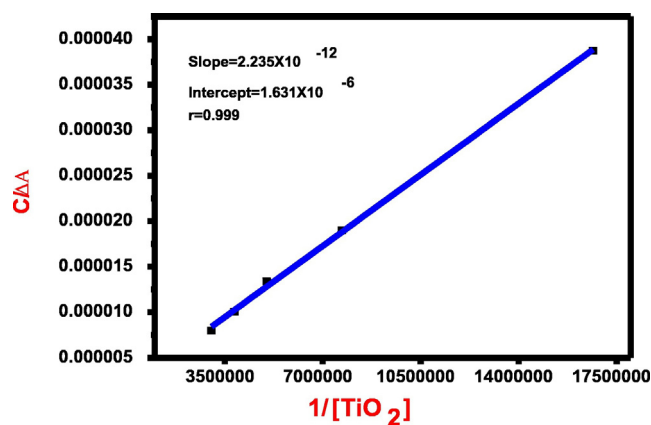


Fig. 5. The plot of  $C/\Delta A$  versus  $1/[TiO_2]$ .

is the fluorescence quantum yield of the donor in the absence of acceptor.  $J$  is the overlap integral between the donor emission and acceptor absorption [19] and is calculated using an equation given below

$$J = \int_0^{\infty} F_d(\lambda) \varepsilon_a(\lambda) \lambda^4 d\lambda \quad (7)$$

where  $F_d(\lambda)$  is the fluorescence intensity of donor in the wavelength range  $\lambda$  to  $\lambda + d\lambda$ , with total intensity normalized to unity and  $\varepsilon_a(\lambda)$  is the extinction co-efficient of the acceptor at  $\lambda$ .

Table 1

Values of absorbance of HMP molecule at its maximum absorbance wavelength for different concentrations of TiO<sub>2</sub> NPs and association constant ( $k_a$ ) of HMP molecule with TiO<sub>2</sub> NPs in the ground state.

TiO <sub>2</sub> NPs concentration (μM/L)	Absorbance (a, u)	Association constant $k_a$ (M <sup>-1</sup> )
0.00	2.491	$0.731 \times 10^6$
0.06	2.233	
0.13	1.965	
0.20	1.744	
0.26	1.495	
0.33	1.237	

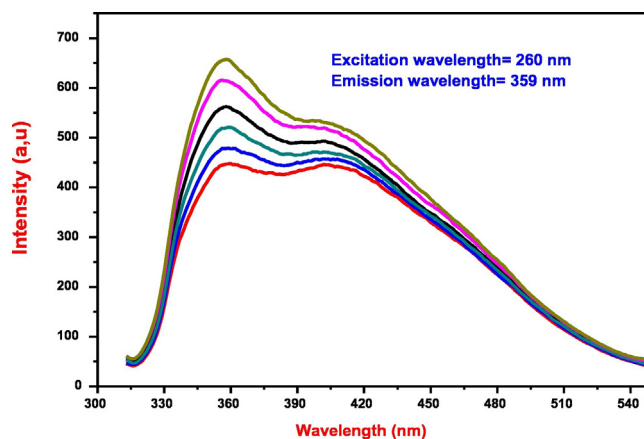


Fig. 6. The fluorescence spectra of HMP molecule in ethanol solvent for different concentrations of TiO<sub>2</sub> NPs.

Knowing the values of  $E$  and  $R_0$ , the distance between acceptor and donor  $r_0$  is calculated using an equation as given below

$$E = \frac{R_0^6}{R_0^6 + r_0^6} \quad (8)$$

The rate of energy transfer between the donor and acceptor [33] is calculated using an equation as given below

$$k_{ET} = \frac{1}{\tau_D} \left( \frac{R_0}{r_0} \right)^6 \quad (9)$$

where  $\tau_D$  is the fluorescence lifetime of the donor in the absence of acceptor.

### 3. Results and discussion

The absorption spectrum of TiO<sub>2</sub> NPs in ethanol solvent is shown in Fig. 2 and it shows the absorption maxima at 345 nm. The emission spectrum of TiO<sub>2</sub> NPs in an ethanol solvent is shown in Fig. 3. The absorption spectra of HMP molecule in an ethanol solvent for different concentrations of TiO<sub>2</sub> NPs (0.00 μM/L, 0.06 μM/L, 0.13 μM/L, 0.20 μM/L, 0.26 μM/L and 0.33 μM/L) were recorded and is shown in Fig. 4. From Fig. 4, we observed that the absorption maxima is at 260 nm. Further, we noticed that by increasing in TiO<sub>2</sub> NPs concentrations there is a decrease in absorbance value at maximum absorbance wavelength; it indicates that there is an interaction of HMP molecule with TiO<sub>2</sub> NPs. Further, we observed that by adding different concentrations of TiO<sub>2</sub> NPs solution to HMP molecule, the shape and band maxima of

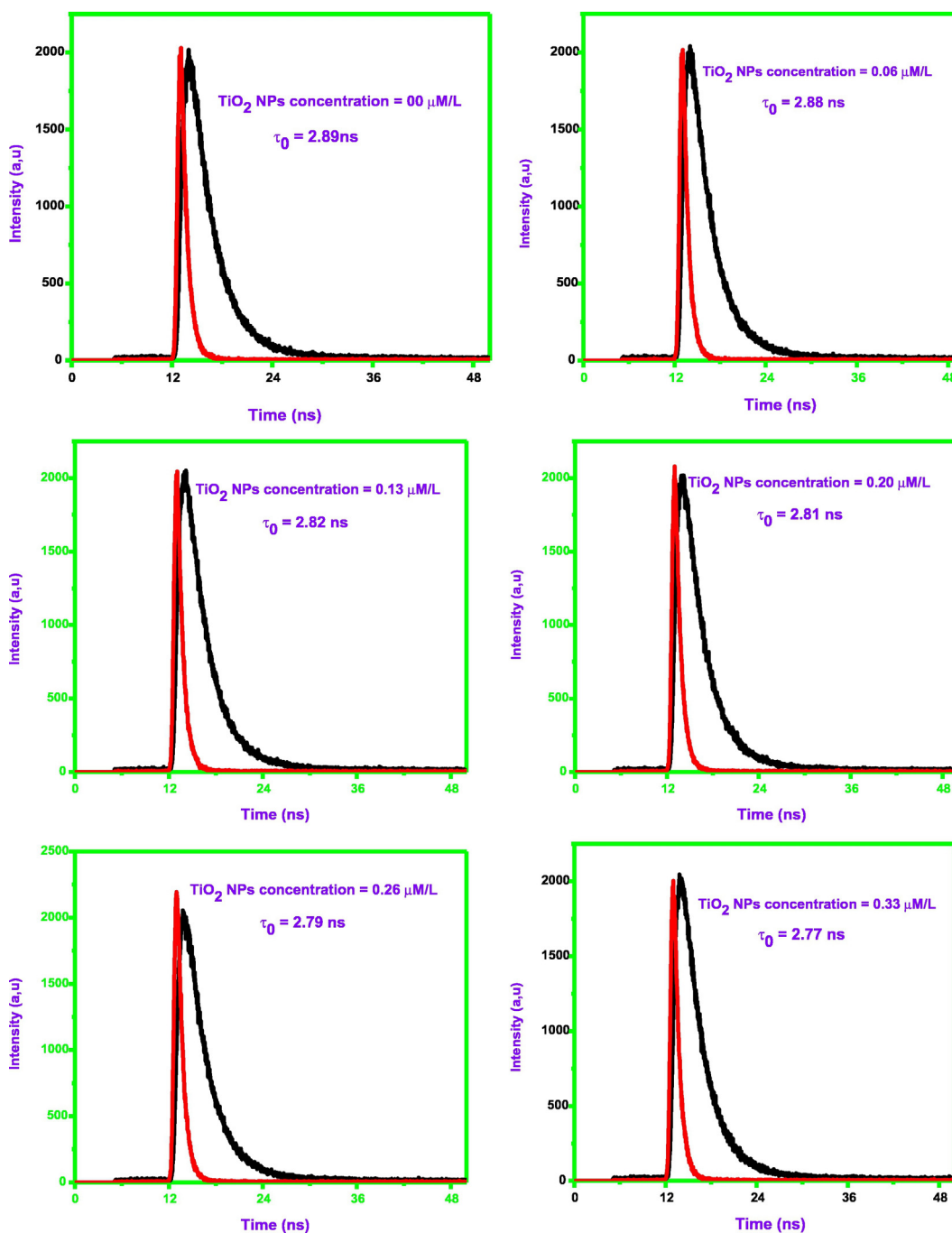


Fig. 7. The fluorescence lifetime decay curve for HMP molecule in ethanol solvent for different concentrations of TiO<sub>2</sub> NPs.

**Table 2**

Values of fluorescence intensity and fluorescence lifetime of HMP molecule in ethanol solvent for different concentrations of TiO<sub>2</sub> NPs.

TiO <sub>2</sub> NPs concentration (μM/L)	Fluorescence intensity (a, u)	Fluorescence lifetime (ns)
0.00	661.713	2.89
0.06	615.182	2.88
0.13	557.945	2.82
0.20	519.716	2.81
0.26	476.024	2.79
0.33	451.338	2.77

absorption spectra of HMP molecule remains unchanged. This inference that there is no possibility of the ground-state complex formation between HMP fluorophore and TiO<sub>2</sub> NPs. The plot of  $C/\Delta A$  versus  $1/[TiO_2]$  according to Benesi–Hildebrand equation [Eq. (1)] was found to be linear with good correlation coefficient and is shown in Fig. 5. From the slope and intercept of this plot, the association constant ( $k_a$ ) value is calculated. Values of absorbance of HMP molecule at its maximum absorbance wavelength for different concentrations of TiO<sub>2</sub> NPs and association constant ( $k_a$ ) of HMP molecule with TiO<sub>2</sub> NPs in the ground state is shown in Table 1. From Table 1, we observed the high value of  $k_a$  which may infer that there will be more interaction of TiO<sub>2</sub> NPs with HMP molecule.

The fluorescence spectra and fluorescence lifetime decay curve for HMP molecule in ethanol solvent with varying concentration of TiO<sub>2</sub> NPs are shown in Fig. 6 and Fig. 7 respectively. Values of fluorescence intensity and fluorescence lifetime of HMP molecule for different concentrations of TiO<sub>2</sub> NPs are shown in Table 2. From Table 2, we observed that the fluorescence intensity and fluorescence lifetime of HMP molecule decrease with increase in the concentration of TiO<sub>2</sub> NPs. This inference that the fluorescence quenching of HMP molecule by TiO<sub>2</sub> NPs is purely dynamic quenching. The plots  $F_0/F$  versus  $[TiO_2]$  and  $\tau_0/\tau$  versus  $[TiO_2]$  were plotted for steady state and transient state methods according to S-V equation [Eq. (2) and Eq. (3)] are found to be linear with intercept nearly unity and are shown in Fig. 8. Values of the slope, intercept, the correlation coefficient of S-V plot for steady state and transient state methods are shown in Table 3. From Table 3, it is observed that good correlation coefficient is obtained in both the cases. The quenching rate parameter ( $k_q$ ) for steady state and transient state methods are calculated using the values of S-V constant and fluorescence lifetime of HMP molecule without TiO<sub>2</sub> NPs and these values are also shown in Table 3.

The plot of  $\log \frac{F_0 - F}{F}$  versus  $\log [TiO_2]$  was plotted according to the binding constant formula [Eq. (4)] are found to be linear with good

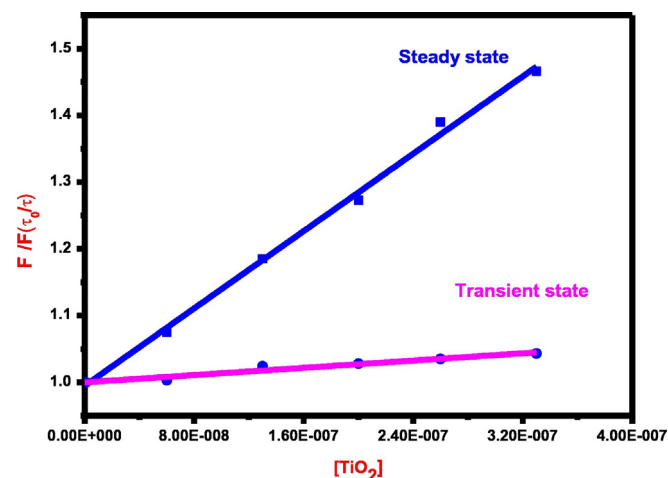


Fig. 8. S-V plot of HMP molecule for steady state and transient state methods.

**Table 3**

Values of slope, intercept and correlation coefficients of S-V plot, quenching rate parameter ( $k_q$ ) for steady state and transient state methods.

Method	Slope $K_{SV} \times 10^6$ ( $M^{-1}$ )	Intercept	Correlation coefficient (r)	Quenching rate parameter $k_q \times 10^{15}$ ( $M^{-1} s^{-1}$ )
Steady state	1.454	1.009	0.996	0.400
Transient state	1.360	0.999	0.969	0.470

correlation coefficient and is shown Fig. 9. Slope and intercept of this plot gives the number of binding sites and binding constant respectively. The values of fluorescence intensity for different quencher concentrations,  $\log[(F_0 - F)/F]$ ,  $\log[TiO_2]$ , binding constant ( $k_b$ ) and a number of binding sites ( $n$ ) are shown in Table 4. From Table 4, we observed that one binding site exists in HMP molecule for TiO<sub>2</sub> NPs.

The absorption spectrum of TiO<sub>2</sub> NPs and emission spectrum of HMP molecule are shown in Fig. 10. From Fig. 10, we observed that there is an overlap between these two spectra, it is inferred that there is possibility of energy transfer between the HMP molecule and TiO<sub>2</sub> NPs. The energy transfer efficiency ( $E$ ) is estimated using an Eq. (5) and these values are shown in Table 5. The value of critical energy transfer distance ( $R_0$ ) is calculated using an Eq. (6) and is found to be 20.82 Å. Using the value of orientation factor relating to the geometry of donor–acceptor dipoles ( $2/3$ ), refractive index of ethanol solvent ( $n = 1.36$ ) and fluorescence quantum yield of HMP molecule in the absence of TiO<sub>2</sub> NPs ( $\phi = 0.0123$ ), the value of  $J$  can be calculated by Eq. (7) and it is found to be  $3.852 \times 10^{-14} M^{-1} cm^{-1} nm^4$ . Binding distance ( $r_0$ ) between HMP molecule and TiO<sub>2</sub> NPs is estimated using an Eq. (8) and shown in Table 5. From Table 5, it is observed that value of  $r_0$  is smaller

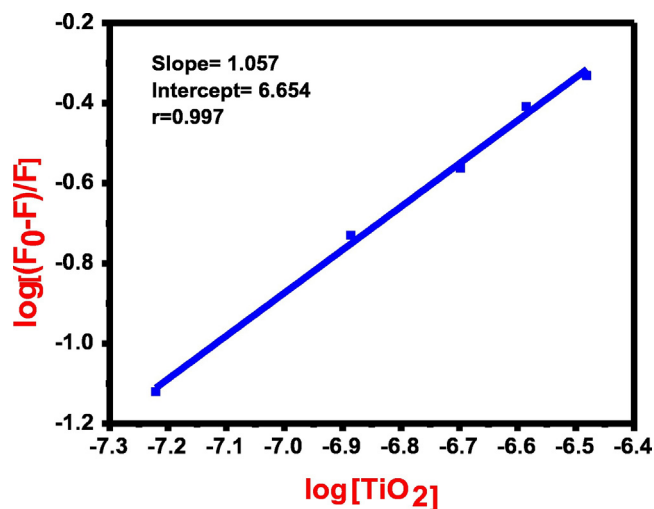


Fig. 9. Plot of  $\log [(F_0 - F)/F]$  versus  $\log [TiO_2]$ .

**Table 4**

Values of fluorescence intensity for different quencher concentrations,  $\log [(F_0 - F)/F]$ ,  $\log [TiO_2]$ , binding constant ( $k_b$ ) and number of binding sites ( $n$ ).

TiO <sub>2</sub> NPs concentration (μM/L)	Fluorescence intensity (a, u)	$\log[(F_0 - F)/F]$	$\log [TiO_2]$	Binding constant $k_b$ ( $M^{-1}$ )	Number of binding sites ( $n$ )
0.00	661.713	-2.8230	...	$4.5 \times 10^6$	1.07
0.06	615.182	-1.1210	-7.221		
0.13	557.945	-0.7300	-6.886		
0.20	519.716	-0.5630	-6.698		
0.26	476.024	-0.4089	-6.585		
0.33	451.338	-0.3316	-6.481		

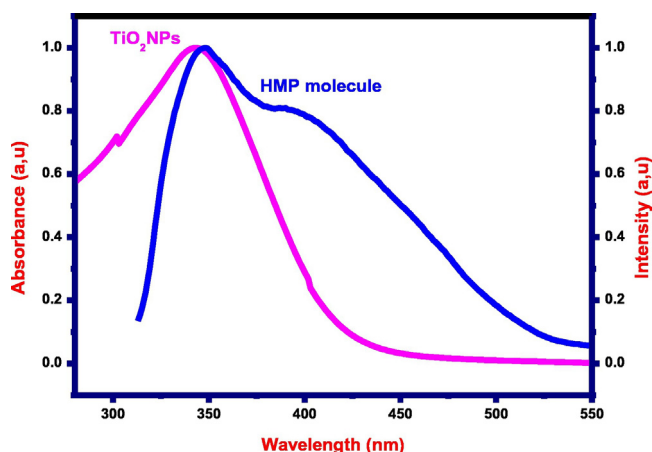


Fig. 10. Absorption spectrum of TiO<sub>2</sub> NPs and emission spectrum of HMP molecule without TiO<sub>2</sub> NPs.

than 70 Å, this is in accordance with Forster's non-radiative energy transfer theory, suggesting a probability of energy transfer from HMP molecule to TiO<sub>2</sub> NPs. The rate of energy transfer between the HMP molecule and TiO<sub>2</sub> NPs is calculated using an Eq. (9) and these values are shown in Table 5.

Due to the high absorbing power of HMP molecule on TiO<sub>2</sub> NPs, it is possible to attach HMP molecule on TiO<sub>2</sub> NPs which will be useful to sensitize the TiO<sub>2</sub> material for solar energy conversion. In addition, present investigations of HMP molecule and TiO<sub>2</sub> NPs are may be useful in biological sensing, medical diagnosis etc.

#### 4. Conclusion

From ongoing results, we summarized that

- Values of absorption, fluorescence intensity and fluorescence lifetime of HMP molecule decreases with the increase of TiO<sub>2</sub> NPs concentration.
- The high value of  $k_a$  indicates that there is more interaction of TiO<sub>2</sub> NPs with HMP molecule.
- The fluorescence quenching of HMP molecule follows the linear S-V relation and it is due to purely dynamic quenching process.
- One binding site exists in HMP molecule for TiO<sub>2</sub> NPs.
- Fluorescence quenching in HMP molecule by TiO<sub>2</sub> NPs is due to energy transfer from HMP molecule to TiO<sub>2</sub> NPs.

From the above findings, it is possible to attach HMP molecule on TiO<sub>2</sub> NPs which will be useful to sensitize the TiO<sub>2</sub> material for solar energy conversion. In addition, present investigations of HMP molecule and TiO<sub>2</sub> NPs are may be useful in biological sensing, medical diagnosis etc.

Table 5

Values of energy transfer efficiency ( $E$ ), distance between acceptor and donor ( $r_0$ ) and rate of energy transfer between acceptor and donor ( $k_{ET}$ ) of HMP molecule for different concentrations of TiO<sub>2</sub> NPs.

TiO <sub>2</sub> NPs concentration ( $\mu\text{M/L}$ )	Energy transfer efficiency ( $E$ )	Distance between acceptor and donor ( $r_0$ ) ( $\text{\AA}$ )	Rate of energy transfer between acceptor and donor ( $k_{ET}$ ) ( $10^9 \times \text{s}^{-1}$ )
0.06	0.0703	13.46	04.75
0.13	0.1550	12.00	09.45
0.20	0.2145	11.45	12.62
0.26	0.2806	10.96	16.30
0.33	0.3179	10.71	18.70

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#### References

- [1] T. Benn, P. Westerhoff, Nanoparticle silver released into water from commercially available sock fabrics, *Environ. Sci. Technol.* 42 (2008) 4133.
- [2] A. Weir, P. Westerhoff, L. Fabricius, N. Goetz, Titanium dioxide nanoparticles in food and personal care products, *Environ. Sci. Technol.* 46 (2012) 2242.
- [3] R. Liu, X. Wei, D. Tao, Y. Zhao, Study of preparation and tribological properties of rare earth nanoparticles in lubricating oil, *Tribol. Int.* 43 (2010) 1082.
- [4] Q.H. Zeng, A.B. Yu, G.Q. Lu, Max, D.R. Paul, Clay-based polymer nanocomposites, *Research and Commercial Development*, 5, 2005, p. 1574.
- [5] M. Skocaj, M. Filipic, J. Petkovic, S. Nova, Titanium dioxide in our everyday life; is it safe? *Radiol. Oncol.* 45 (2011) 227–247.
- [6] C. Burda, Y. Lou, Enhanced nitrogen doping in TiO<sub>2</sub> nanoparticles, *Nano Lett.* 3 (2003) 1049.
- [7] B. Tan, Y. Wu, Dye-sensitized solar cells based on anatase TiO<sub>2</sub> nanoparticle/nanowire composites, *J. Phys. Chem. B* 110 (2006) 15932.
- [8] S.M. Hunagund, V.R. Desai, J.S. Kadavevarmath, D.A. Barretto, S.K. Vootla, A.H. Sidarai, Biogenic and chemogenic synthesis of TiO<sub>2</sub> NPs via hydrothermal route and their antibacterial activities, *RSC Adv.* 6 (2016) 97438.
- [9] K. Murugan, D. Dinesh, K. Kavitha, Hydrothermal synthesis of titanium dioxide nanoparticles: mosquitocidal potential and anticancer activity on human breast cancer cells (MCF-7), *J. Parasitol. Res.* 115 (2016) 1085.
- [10] J. Alvarez-Builla, Vaquero and Barleuenga, *Modern Heterocyclic Chemistry*, UK, 2011.
- [11] M. Asif, Some recent approaches of biologically active substituted Pyridazine and Phthalazine drugs, *Curr. Med. Chem.* 19 (2012) 2984.
- [12] S. Dubey, P.A. Bhosle, Pyridazinone: an important element of pharmacophore Possessing broad spectrum of activity, *Med. Chem. Res.* (2015) <http://dx.doi.org/10.1007/s00044-15-1398-5>.
- [13] S. Bahceli, H. Gokce, Study on spectroscopic and quantum chemical calculations of levosimendan, *Pure Appl. Phys.* 52 (2014) 224.
- [14] H. Gokce, S. Bahceli, Spectroscopic and quantum chemical studies on Bromopyrazone, *Spectrochim. Acta A* 133 (2014) 741.
- [15] D. Avci, S. Bahceli, O. Tamer, Y. Atalay, Comparative study of DFT/B3LYP, B3PW91 and HSEH1PB6 methods applied to molecular structures and spectroscopic and electronic properties of flufenpyr and amipizone, *Can. J. Chem.* 93 (2015) 1147.
- [16] S.M. Soliman, J. Albering, M.A.M. Abu-Youssef, Molecular structure, spectroscopic properties, NLO, HOMO-LUMO and NBO analyses of 6-hydroxy-3(2H)-Pyridazinone, *Spectrochim. Acta A* 136 (2015) 1086.
- [17] V.R. Desai, A.H. Sidarai, S.M. Hunagund, M. Basanagouda, R.M. Melavanki, R.H. Fattepur, J.S. Kadavevarmath, Steady state absorption and fluorescence study: estimation of ground and excited state dipole moments of newly synthesized pyridazin-3(2H)-one derivatives, *J. Mol. Liq.* 223 (2016) 141.
- [18] V.R. Desai, S.M. Hunagund, M. Basanagouda, J.S. Kadavevarmath, A.H. Sidarai, Solvent effects on the electronic absorption and fluorescence spectra of HNP: estimation of ground and excited state dipole moments, *J. Fluoresc.* 26 (2016) 1391.
- [19] J.R. Lackowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York, 1983.
- [20] J.S. Kadavevarmath, G.H. Malimath, R.M. Melavanki, N.R. Patil, Static and dynamic model fluorescence quenching of laser dye by carbon tetrachloride in binary mixtures, *Spectrochim. Acta A* 117 (2014) 630.
- [21] V.R. Desai, S.M. Hunagund, M. Basanagouda, J.S. Kadavevarmath, J. Thipperudrappa, A.H. Sidarai, Spectroscopic studies on newly synthesized 5-(2-hydroxy-5-methoxyphenyl)-2-phenyl-2H-pyridazin-3-one molecule, *J. Mol. Liq.* (2016) <http://dx.doi.org/10.1016/j.molliq.2016.11.080>.
- [22] A.H. Sidarai, V.R. Desai, S.M. Hunagund, M. Basanagouda, J.S. Kadavevarmath, Effect of solvent polarity on the fluorescence quenching of TMC molecule by aniline in benzene-acetonitrile mixtures, *Can. J. Phys.* (2016) <http://dx.doi.org/10.1139/cjp-2016-0213>.
- [23] A.H. Sidarai, V.R. Desai, S.M. Hunagund, M. Basanagouda, J.S. Kadavevarmath, Fluorescence quenching of DMB by aniline in benzene-acetonitrile mixture, *Int. Lett. Chem. Phys. Astron.* 65 (2016) 32.
- [24] J. Olmsted, Oxygen quenching of fluorescence of organic dye molecules, *J. Chem Phys Lett.* 26 (1974) 33.
- [25] U.P. Raghavendra, M. Basanagouda, A.H. Sidrai, J. Thipperudrappa, Spectroscopic investigations on the interaction of biologically active 4-aryloxyethyl coumarins with TiO<sub>2</sub> nanoparticles, *J. Mol. Liq.* 222 (2016) 601.
- [26] H.R. Deepa, H.M. Suresh Kumar, M. Basanagouda, J. Thipperudrappa, Influence of silver nanoparticles on absorption and fluorescence properties of laser dyes, *Can. J. Phys.* 92 (2014) 163.

- [27] P. Manikandan, V. Ramakrishnan, Spectral investigations on N-(2-methyl thiophenyl) 2-hydroxy-1-naphthalimine by silver nanoparticles, *J. Fluoresc.* 21 (2011) 693.
- [28] J. Keizer, Diffusion effects on rapid bimolecular chemical reactions, *Chem. Rev.* 87 (1987) 167.
- [29] M.R. Eftink, C.A. Ghiron, Fluorescence quenching studies with proteins, *Anal. Biochem.* 114 (1981) 199.
- [30] M. Basanagouda, M.V. Kulkarni, Novel one-pot synthesis for 2,5-diaryl and 5-aryl-pyridazin-3(2H)-ones, *Synth. Commun.* 41 (2011) 2569.
- [31] H.A. Benesi, J.H. Hildebrand, A spectrophotometric investigation of the interaction of iodine with aromatic hydrocarbons, *J. Am. Chem. Soc.* 71 (1949) 2703.
- [32] Y.J. Hu, Y. Liu, J.B. Wang, X.H. Xiao, S.S. Qu, Study of the interaction between monoammonium glycyrrhizinate and bovine serum albumin, *J. Pharm. Biomed. Anal.* 36 (2004) 915.
- [33] D. Seth, D. Chaktabarthy, A. Chakrabarthy, N. Sarkar, Study of energy transfer from 7-amino coumarin donors to rhodamine 6G acceptor in non-aqueous reverse micelles, *Chem. Phys. Lett.* 401 (2005) 546.