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Influence of concentrations of TiO_2 nanoparticles on spectroscopic properties of a novel HMPP molecule

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ABSTRACT

The influence of concentrations of titanium dioxide (TiO_2) nanoparticles (NPs) on spectroscopic properties of a novel 3(*2H*)-pyridazinone derivative; 5-(2-hydroxy-5-methoxy-phenyl)-2-phenyl-2H-pyridazin-3-one (HMPP) molecule in ethanol as a solvent has been investigated at room temperature. The increase in TiO_2 NPs concentration causes a decrease in the values of absorption, fluorescence intensity and fluorescence lifetime of HMPP molecule. The association constant k_a of HMPP molecule with TiO_2 NPs in the ground state is estimated using the Benesi–Hildebrand relation. A linear Stern–Volmer (S-V) plot is obtained in steady state and transient state studies. In addition, we have estimated the binding constant and number of binding sites. Results reveal that there is a strong interaction between investigated molecule with TiO_2 NPs, fluorescence quenching in the said system is purely dynamic and also there exist one binding site in HMPP molecule for TiO_2 NPs.

1. Introduction

In recent years, there has been considerable interest in semiconductor nanocrystals due to their unique size and shape dependent properties, a large surface-to-volume ratio, special optical and electrical properties as compared to those of the bulk materials [1–3]. As one of the most important ternary chalcogenides, TiO_2 is an intriguing functional material because of its promising applications in photovoltaic and photocatalytic fields [4,5]. Recently, S. M. Hunagund et al. reported that the TiO_2 NPs shows potent antibacterial activity against the multi-drug resistant microorganisms like *Staphylococcus aureus* and *Escherichia coli* [6]. It has been reported that the TiO_2 NPs interact with biomolecules of the bacteria cells [7], it provides a better understanding of the cytotoxicity of oxide NPs. Also, it is reported that the TiO_2 NPs interact with poly (lactic-*co*-glycolic acid) in order to study their cytotoxicity [8]. Similar works shine on the interaction between metal oxide nanoparticles with biomolecules in the field of biological applications.

The phenomenon of fluorescence quenching competes with the spontaneous emission and causes the reduction in the fluorescence intensity and lifetime of the fluorescence molecules. The electronic excitation energy of an excited molecule is transferred to a quencher molecule via, several mechanisms such as resonance, molecular rearrangement, charge transfer etc., The interaction between fluorophore and quenching agent can modify the emission characteristics of fluorophore or of the fluorophore-quencher system (dynamic mechanism) or it can become totally non-fluorescent (static mechanism). Fluorescence quenching of organic molecules in solution by various quenchers like silver nanoparticles [9], titanium dioxide nanoparticles [10,11], SnO_2 NPs [12], aniline [13,14] and carbon tetrachloride [15] etc. have been studied by several investigators using steady state and the transient state methods. The applications of quenching phenomenon are very useful in physical science, chemical science and medical science [16,17].

The 3(*2H*)-pyridazinones are the pyridazine derivatives which contain two adjacent nitrogen atoms at the first and second positions in a six-membered ring and a carbonyl group at the third position and they have different functionalities in their structure. They show broad absorption and fluorescence spectra. Pyridazinones are biologically most important and applicable subset of pyridazines and therefore they have been the focus of intense study in the field of medicinal chemistry. They exhibit diverse biological activities such as antimicrobial, analgesic, anti-inflammatory, antipyretic, antihypertensive, anticancer, antituberculosis, antiplatelet, antidiabetic, adrenoreceptor antagonist, cardiotonic, COX inhibitors and acetylcholinesterase activities which have been reviewed recently [18]. The chloridazon and pyridaben are the derivatives of pyridazin-3(*2H*)-ones used in agriculture as weedicidal and muticidal agents [19,20]. Recently, our group reported the spectroscopic properties of novel pyridazin-3(*2H*)-one derivatives using solvatochromic approaches [21–23]. In this work, we have studied

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the dependence of fluorescence intensity for pyridazin-3(*2H*)-one derivative 5-(2-hydroxy-5-methoxy-phenyl)-2-phenyl-2H-pyridazin-3-one (HMPP) molecule on titanium dioxide (TiO_2) nanoparticles (NPs) in ethanol as a solvent at room temperature.

2. Experimental

2.1. Materials and methods

5-(2-hydroxy-5-methoxy-phenyl-2-phenyl)-2H-pyridazin-3-one (HMPP) was synthesized as per the procedure mentioned in the literature [24], and its molecular structure is shown in Fig. 1. The solvent ethanol was of spectroscopic grade and is purchased from S.D. Fine Chemicals Ltd., India. TiO_2 NPs were purchased from HiMedia Laboratories Pvt. Ltd. India. In order to prepare quencher, we have used TiO_2 NPs in 5 ml of ethanol solvent (1×10^{-5} M). Solutions were prepared to keep the concentration of solute HMPP fixed (1×10^{-5} M) and varying TiO_2 NPs concentrations (0.00 μM, 0.06 μM, 0.13 μM, 0.20 μM, 0.26 μM and 0.33 μM).

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

2.2. Benesi–Hildebrand relation

The change in the absorption value of HMPP molecule by adding different concentrations of TiO_2 NPs is analyzed using the Benesi–Hildebrand relation [25] and is given by

$$\frac{C}{\Delta A} = \frac{1}{\Delta\varepsilon} + \frac{1}{\Delta\varepsilon k_a[TiO_2]} \tag{1}$$

where k_a - Association constant.C - Concentration of HMPP molecule.ΔA - Change in absorbance of HMPP molecule with and without TiO_2 NPs at its maximum absorption wavelength.$\Delta\varepsilon$ - Change in absorption coefficient.

2.3. Stern-Volmer [S-V] relation

The change in the fluorescence intensity and fluorescence lifetime of HMP molecule by adding different concentrations of TiO_2 NPs is analyzed using the S-V relation [26] and is given by.

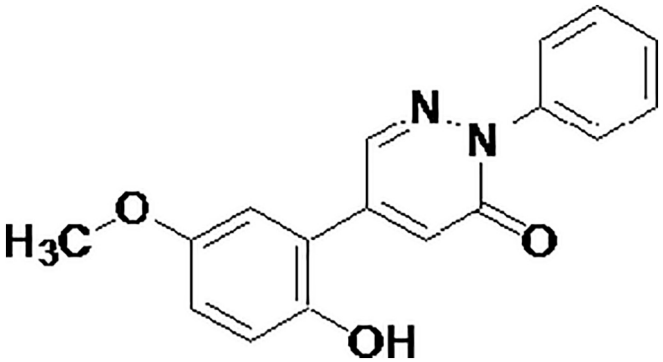

Fig. 1. Molecular structure of HMPP molecule.

For steady state

$$\frac{F_0}{F} = 1 + K_{SV}[TiO_2] \tag{2}$$

For transient state

$$\frac{\tau_0}{\tau} = 1 + K'_{SV}[TiO_2] \tag{3}$$

where F_0 - Fluorescence intensity of solute without a quencher.F - Fluorescence intensity of solute with a quencher.τ_0 - Fluorescence lifetime of solute without a quencher.τ - Fluorescence lifetime of solute with a quencher.$[TiO_2]$ - TiO_2 NPs 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.$k_q(k'_q)$ is quenching rate parameter.

2.4. Binding constant formula

The relationship between fluorescence intensity of HMPP molecule and concentration of TiO_2 NPs can be described by the binding constant formula [27] and is given by

$$\log\frac{F_0 - F}{F} = \log k_b + n\,\log[TiO_2] \tag{4}$$

where k_b - Binding constant.n - Number of the binding sites.

3. Results and discussion

3.1. Absorption spectra of TiO_2 NPs and HMPP molecule

The absorption spectrum of TiO_2 NPs in ethanol as a solvent is shown in Fig. 2; and it shows the absorption maxima at 345 nm. The absorption spectra of HMPP molecule in ethanol solvent for different concentrations of TiO_2 NPs is shown in Fig. 3. From Fig. 3 it is observed that the absorption value of HMPP molecule decreases with increase in the TiO_2 NPs concentrations. It inferred that there is an interaction between the HMPP molecule and TiO_2 NPs. The change in the absorption value of HMPP molecule by adding different concentrations of TiO_2 NPs is analyzed using the Benesi–Hildebrand relation [Eq. (1)]. The plot of $C/\Delta A$ versus $1/[TiO_2]$ according to Benesi–Hildebrand relation [Eq. (1)] was found to be linear with good correlation coefficient and is shown in

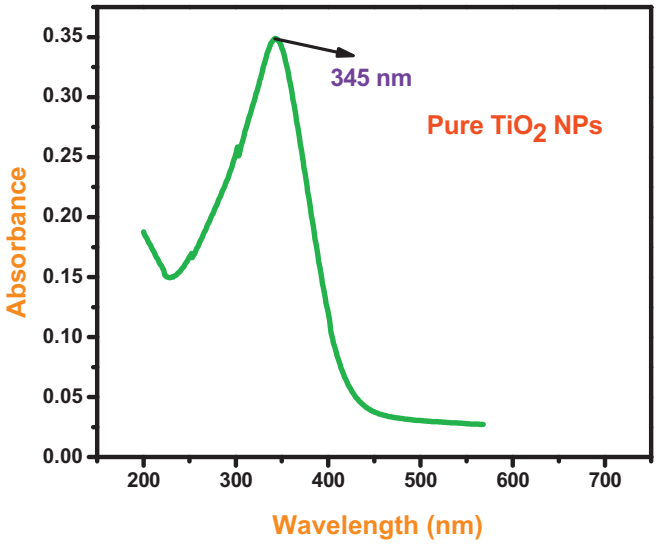

Fig. 2. Absorption spectrum of TiO_2 NPs in ethanol as a solvent.

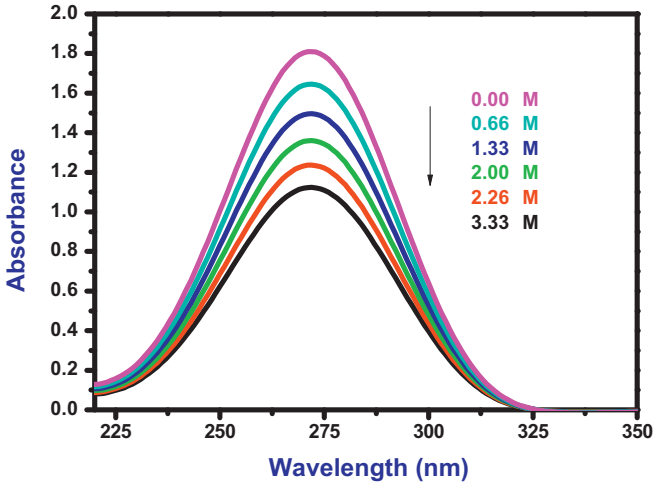

Fig. 3. The absorption spectra of HMPP molecule for different concentrations of TiO_2 NPs in ethanol as a solvent.

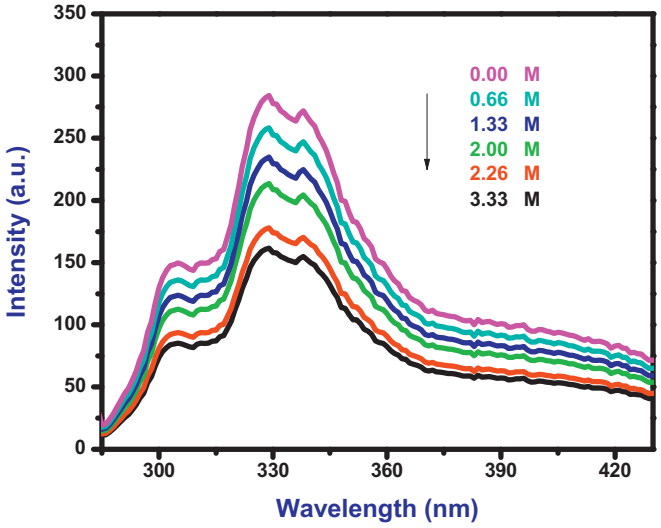

Fig. 5. Fluorescence spectra of HMPP molecule in ethanol as a solvent for different concentrations of TiO_2 NPs.

Fig. 4. From the slope and intercept of this plot, the association constant (k_a) value is calculated. It is found to be $1.645 \times 10^6\ M^{-1}$. The higher k_a value indicates that there is a more interaction between TiO_2 NPs and the investigated HMPP molecule.

3.2. The fluorescence spectrum of HMPP molecule

The fluorescence spectrum of HMPP molecule in ethanol solution is recorded by exciting the sample at its maximum absorption wavelength i.e. 273 nm. The Fluorescence spectrum of HMPP molecule for various concentrations of TiO_2 NPs is shown in Fig. 5. From Fig. 5, it is observed that the fluorescence intensity of HMPP molecule decreases with increase in TiO_2 NPs concentration. The values of fluorescence intensity of HMPP molecule for different concentrations of TiO_2 NPs are shown in Table 1. The fluorescence intensity of HMPP molecule by adding TiO_2 NP_S is analyzed using the Stern-Volmer relation [Eq. (2)]. The plot F_0/F versus $[TiO_2]$ for steady state method according to S-V relation [Eq. (2)] is found to be linear with intercepts nearly unity and is shown in Fig. 6. Values of the slope, intercept, and a correlation coefficient of S-V plot for steady state method are shown in Table 2. From Table 2 it is observed that good correlation coefficient is obtained. The quenching rate parameter (k_q) in steady state method is shown in Table 2.

3.3. Fluorescence lifetimes of HMPP molecule

The fluorescence lifetime decay curves for HMPP molecule with and without TiO_2 NPs are shown in Fig. 7. Values of fluorescence lifetime of HMPP molecule for various concentrations of TiO_2 NPs along with their corresponding χ^2 values are shown in Table 1. The fluorescence lifetimes of HMPP molecule by adding different concentrations of TiO_2 NP_S is analyzed using the Stern-Volmer relation [Eq. (3)]. The plot of τ_0/τ versus $[TiO_2]$ in transient state methods according to S-V relation [Eq. (3)] is found to be linear with intercepts nearly unity and is shown in Fig. 8. Values of the slope, intercept, the correlation coefficient of S-V plot in transient state method is shown in Table 2. From Table 2 it is observed that good correlation coefficient is obtained.

From Sections 3.2 and 3.3 it is observed that fluorescence intensities and fluorescence lifetimes of HMPP molecule decrease with increase in TiO_2 NPs concentrations and also linear Stern-Volmer (S-V) plot in steady state and transient state methods indicate the presence of dynamic quenching.

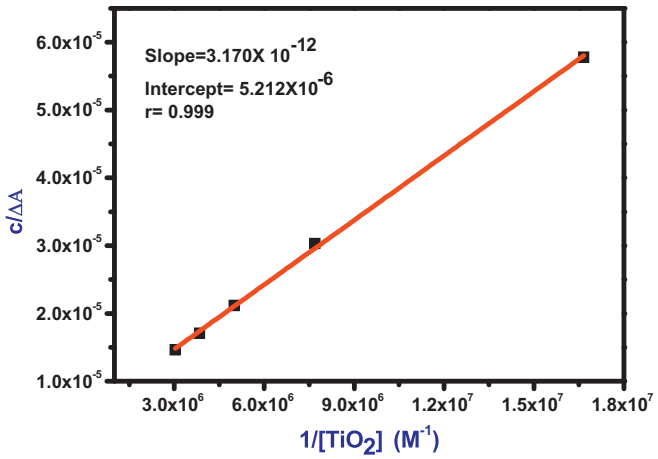

Fig. 4. The plot of $C/\Delta A$ versus $1/[TiO_2]$.

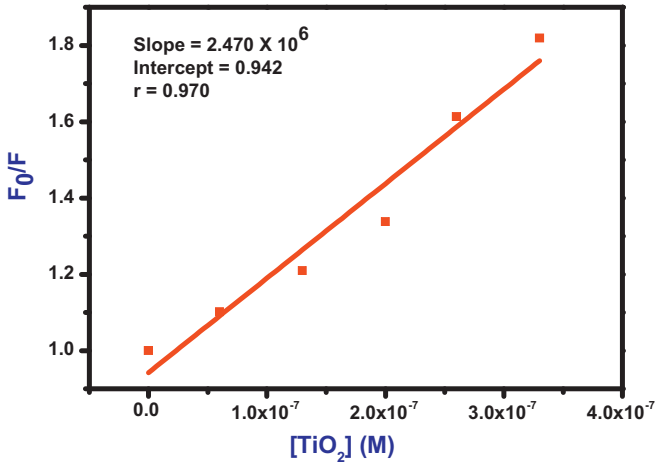

Fig. 6. S-V plot for HMPP molecule in steady state.

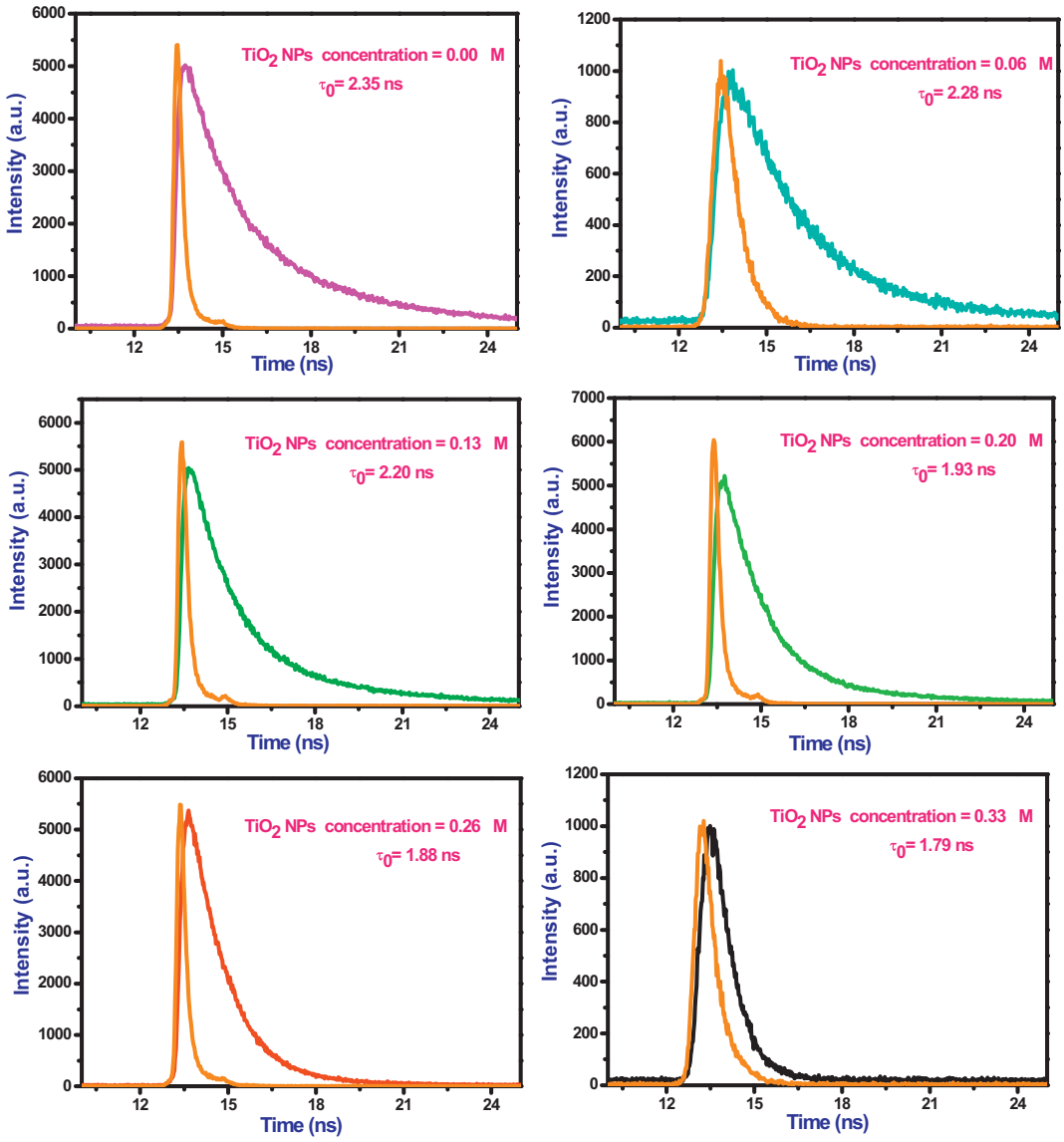

Fig. 7. The fluorescence lifetime decay curves for HMPP molecule for different concentrations of TiO_2 NPs in ethanol as a solvent.

3.4. Binding constant and number of binding sites

Using the values of fluorescence intensity with and without TiO_2 NPs the binding constant and number of binding sites are estimated. The plot of $\log\frac{F_0-F}{F}$ versus $\log[TiO_2]$ was plotted according to binding constant formula [Eq. (4)] is found to be linear with good correlation coefficient and is shown Fig. 9. Slope and intercept of this plot give the number of binding sites and binding constant respectively. The values

Table 1
Values of fluorescence intensity, fluorescence lifetime and Chi-square value of HMPP molecule for different concentrations of TiO_2 NPs in ethanol solvent.

TiO_2 NPs concentration (μM)	Fluorescence intensity (a.u.)	Fluorescence lifetime (ns)	Chi-square (χ^2) value
0.00	283.579	2.35	1.02
0.06	257.195	2.28	1.05
0.13	234.543	2.20	1.08
0.20	211.795	1.93	1.11
0.26	175.808	1.88	1.12
0.33	155.850	1.79	1.10

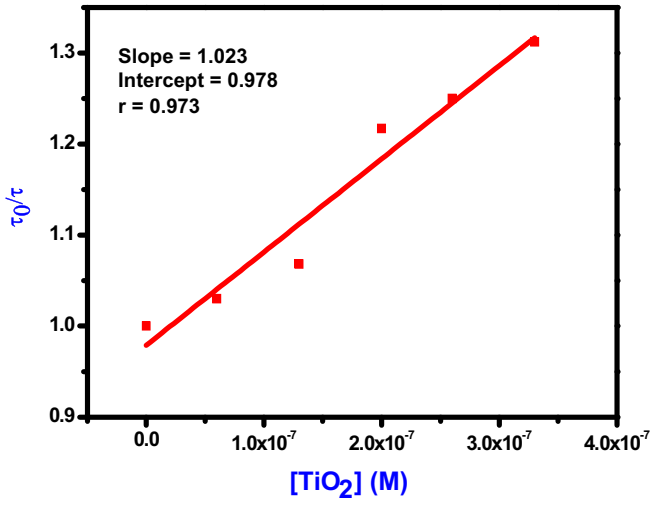

Fig. 8. S-V plot for HMPP molecule in transient state method.

Table 2
Values of slope (K_{SV}), intercept and correlations coefficient (r) of S-V plot, quenching rate parameter (k_q) in steady state and transient state methods.

Method	Slope $[K_{SV} \times 10^6]$ (M^{-1})	Intercept	Correlation coefficient	Quenching rate parameter $[k_q \times 10^{15}]$ $(M^{-1}\ s^{-1})$
Steady state	2.470	0.942	0.970	1.051
Transient state	1.023	0.978	0.973	0.435

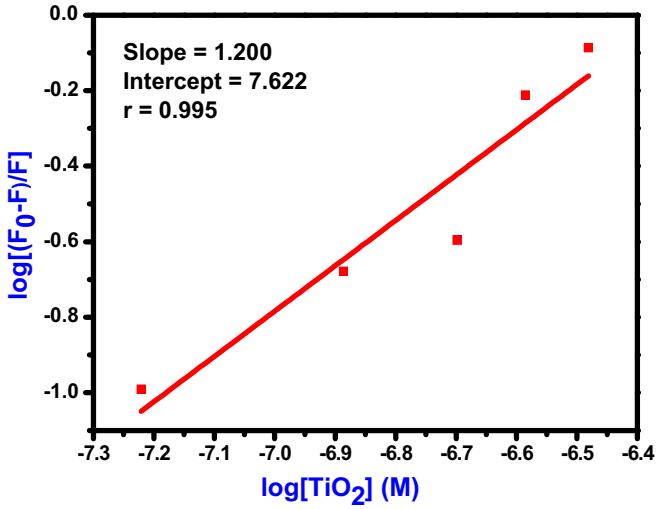

Fig. 9. Plot of log $[(F_0\text{-}F)/F]$ versus log $[TiO_2]$.

of fluorescence intensity for different quencher concentrations, log $[(F_0\text{-}F)/F]$, log $[TiO_2]$, binding constant (k_b) and a number of binding sites (n) are shown in Table 3. From Table 3 we observed that one binding site exists in investigated molecule for TiO_2 NPs.

4. Conclusion

The dependence of fluorescence intensity of a novel pyridazin-3 (*2H*)-one derivative HMPP molecule on titanium dioxide (TiO_2) nanoparticles (NPs) in ethanol as a solvent has been investigated at room temperature. The value of absorption for HMPP molecule decreases with increase in TiO_2 NPs concentration. The large value of association constant indicates that there is a large interaction between HMPP molecule and TiO_2 NPs. The fluorescence intensity and fluorescence lifetime of HMPP molecule decrease with increase in TiO_2 NPs concentration and the obtained S-V plot in both cases are linear. It is inferred that the fluorescence quenching in HMPP molecule by TiO_2 NPs is purely dynamic in nature. Further, we conclude that there is a one binding site exists in the investigated molecule for TiO_2 NPs.

Table 3
Values of fluorescence intensity of HMPP molecule for different concentrations of TiO_2 NPs, log $[(F_0\text{-}F)/F]$, log $[TiO_2]$, binding constant (k_b) and number of binding site (n).

TiO_2 NPs concentration (μM)	Fluorescence intensity (a.u.)	log $[(F_0\text{-}F)/F]$	log $[TiO_2]$	Binding constant $[k_b \times 10^7]$ (M^{-1})	Number of binding site
0.00	283.579	…	…	4.168×10^7	1.200
0.06	257.195	−0.991	−7.221		
0.13	234.543	−0.679	−6.886		
0.20	211.795	−0.596	−6.698		
0.26	175.808	−0.212	−6.585		
0.33	155.850	−0.086	−6.481		

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References

[1] P.K. Samanta, P.R. Chaudhuri, Sci. Adv. Mater. 3 (2011) 919.
[2] Y. Li, G.S. Cheng, L.D. Zhang, J. Mater. Res. 15 (2000) 2305.
[3] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gande, J. Appl. Phys. 79 (1996) 7983.
[4] V.M. Ramakrisnan, M. Natarajan, A. Santhanam, V. Asokan, D. Velauthapillai, J. Mat. Res. Bull. 97 (2018) 351.
[5] S. Lakshmi, R. Renganathan, J. Photochem. Photobiol. A Chem. 88 (1995) 163.
[6] S.M. Hunagund, V.R. Desai, J.S. Kadadevarmath, D.A. Barretto, S.K. Vootla, A.H. Sidarai, RSC Adv. 6 (2016) 97438.
[7] W. Jiang, K. Yang, R.W. Vachet, Baoshan Xing, Langmuir 26 (2010) 18071.
[8] S. Xiong, S. George, H. Yu, R. Damoiseaux, B. France, K.W. Ng, J. Say-Chye Loo, J. Arch. Toxicol. 87 (2013) 1075.
[9] H.R. Deepa, H.M. Suresh Kumar, M. Basanagouda, J. Thipperudrappa, Can. J. Phys. 92 (2014) 163.
[10] U.P. Raghavendra, M. Basanagouda, A.H. Sidrai, J. Thipperudrappa, J. Mol. Liq. 222 (2016) 601.
[11] V.R. Desai, S.M. Hunagund, M.S. Pujar, M. Basanagouda, J.S. Kadadevarmath, A.H. Sidarai, J. Mol. Liq. 233 (2017) 166.
[12] N. Nagarajan, G. Paramaguru, G. Vanitha, R. Renganathan, J. Chem. 2013 (2013) 1.
[13] A.H. Sidarai, V.R. Desai, S.M. Hunagund, M. Basanagouda, J.S. Kadadevarmath, Int. Lett. Chem. Phys. Astron. 65 (2016) 32.
[14] A.H. Sidarai, V.R. Desai, S.M. Hunagund, M. Basanagouda, J.S. Kadadevarmath, Can. J. Phys. 94 (2016) 1125.
[15] J.S. Kadadevarmath, G.H. Malimath, R.M. Melavanki, N.R. Patil, Spectrochim. Acta A 117 (2014) 630.
[16] J. Keizer, Chem. Rev. 87 (1987) 167.
[17] M.R. Eftink, C.A. Ghiron, Anal. Biochem. 114 (1981) 199.
[18] S. Dubey, P.A. Bhosle, Med. Chem. Res. 24 (2015) 3579.
[19] BASF website: www.basf.com.
[20] S. Nara, J. Martinez, C.G. Wermuth, I. Parrot. Syn. Let. 19 (2006) 3185.
[21] V.R. Desai, S.M. Hunagund, M. Basanagouda, J.S. Kadadevarmath, J. Thipperudrappa, A.H. Sidarai, J. Mol. Liq. 225 (2017) 613.
[22] V.R. Desai, A.H. Sidarai, S.M. Hunagund, M. Basanagouda, R.M. Melavanki, R.H. Fattepur, J.S. Kadadevarmath, J. Mol. Liq. 223 (2016) 141.
[23] V.R. Desai, S.M. Hunagund, M. Basanagouda, J.S. Kadadevarmath, A.H. Sidarai, J. Fluoresc. 26 (2016) 1391.
[24] M. Basanagouda, M.V. Kulkarni, Synth. Commun. 41 (2011) 2569.
[25] H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.
[26] J.R. Lackowicz, Principles of Fluorescence Spectroscopy, Plenum Press, New York, 1983.
[27] Y.J. Hu, Y. Liu, J.B. Wang, X.H. Xiao, S.S. Qu, J. Pharm. Biomed. Anal. 36 (2004) 915.