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Analysis of fluorescence quenching of new indole derivative by aniline using Stern–Volmer plots

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Abstract

The fluorescence quenching of 5-methyl-3-phenyl-2-[4′-amino-s-triazolo-3′-yl] indole-5′-hydrazide (MPIH) by aniline quencher in cyclohexane, benzene, toluene and dioxane solvents has been carried out at room temperature with a view to understand the quenching mechanisms. The quenching is found to be appreciable and shows positive deviation in the Stern–Volmer plots. The various quenching parameters have been determined using modified Stern–Volmer equation, which suggests that the sphere of action static quenching model agrees very well with the experimental results and this positive deviation is attributed to the static and dynamic quenching. Further, with the use of the finite sink approximation model, it is concluded that these bimolecular quenching reactions are diffusion limited and the distance parameter R' and mutual diffusion co-efficient D are estimated independently.

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Keywords: Indole; Fluorescence; Quenching; Stern–Volmer plot; Static and dynamic quenching; Diffusion limited

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1. Introduction

The fluorescence quenching phenomenon of organic molecules using external quenchers in liquid phase has been widely studied by various authors to understand the nature of bimolecular reactions taking place both under steady-state and transient conditions [1–6]. This study is very

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important in physical, chemical, biological and medical sciences [6–8]. In bimolecular liquid systems, the fluorescence intensity is hindered due to several mechanisms, such as static and dynamic quenching, excimer and exciplex formation, charge transfer process, etc. [2–4,8,9]. The role of fluorescence quenching can be studied experimentally by determining quenching rate parameters using Stern–Volmer (S–V) plots that are drawn in accordance with the S–V equation:

$$I_0/I = 1 + K_{\mathrm{SV}}[Q] \tag{1}$$

and

$$\tau_0/\tau = 1 + K'_{\mathrm{SV}}[Q], \tag{2}$$

where I_0 and τ_0 are the fluorescence intensity and fluorescence lifetime, I and τ are the fluorescence intensity and fluorescence lifetime in the absence and presence of the quencher concentration $[Q]$, respectively, and K_{SV} (K'_{SV}) is the S–V constant. In many cases, the S–V plots were found to be linear, in which the quenching mechanism is mainly due to the dynamic process, where diffusion process is the dominant one [10,11]. In some cases, the experimental results show positive deviation from the linear S–V relation [1–3,12–14]. This finding may be due to one of the above processes other than or along with diffusion process. Apart from this, the polarity of the solvent medium and the range of quencher concentration are also expected to play a part in this medium [15].

In the present study, we have studied the steady-state fluorescence quenching of the newly synthesized indole derivative 5-methyl-3-phenyl-2-[4′-amino-s-triazolo-3′-yl] indole-5′-hydrazide[MPIH] at room temperature using aniline as a quencher in cyclohexane, dioxane, benzene and toluene solvents, and also by the transient method in toluene solvent to understand the nature of the quenching mechanism.

2. Experimental details

The solute, MPIH was synthesized in our laboratory using standard methods [16,17] and was purified by double re-crystallization using acetone-ethyl alcohol solvents. The molecular structure of MPIH is shown in Fig. 1. The spectroscopic grade solvents (S.D. Fine Chemicals Ltd.) have been used without further purification to prepare the solutions. However, the purity of the solvents was checked by recording the background fluorescence. Spectroscopic grade aniline solvent has been used as a quencher and it was double distilled before use.

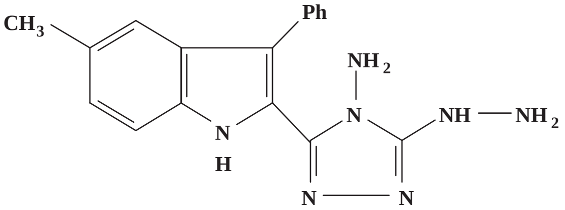

Fig. 1. Molecular structure of 5-methyl-3-phenyl-2-[4′-amino-s-triazolo-3′-yl] indole-5′-hydrazide.

Absorption spectra were recorded in different solvents using UV–visible absorption spectrophotometer (Hitachi model 150-20) at the concentration of $1\times10^{-5}\,\mathrm{mol\,dm^{-3}}$. The steady-state fluorescence spectra were recorded for the same concentration by exciting the sample at 320 nm radiation corresponding to the longer absorption peak using fluorescence spectrophotometer (Hitachi model F-2000) in all the solvents by varying the quencher concentration from 0.00 to $0.10\,\mathrm{mol\,dm^{-3}}$. The fluorescence decays of the solute were recorded without and with quencher in toluene solvent using picosecond time correlated single photon counting technique (TCSPC) (Model 5000U, IBH, UK). The third harmonic picosecond laser pulse of wavelength 310 nm, derived from the mode locked Ti-Sapphire laser (Model Spectra Physics, Tsunami) pumped by Nd-$\mathrm{YVO_4}$ laser was used as an excitation source. The decays were measured at 390 nm corresponding to fluorescence maxima. The data analysis was accomplished by the software DAS-6 (IBH) based on the deconvolution technique using iterative nonlinear least square methods. The quality of the fit is identified by the reduced chi-square value, weighted residuals and the autocorrelation function of the residuals.