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# Excited state isomerization and effect of viscosity- and temperature-dependent torsional relaxation on TICT fluorescence of *trans*-2-[4-(dimethylamino) styryl]benzothiazole

Subit Kumar Saha[a,*], Pradipta Purkayastha[a,*], Asim Bikas Das[b], Surajit Dhara[c]

[a] *Chemistry Group, Birla Institute of Technology and Science, Pilani 333031, Rajasthan, India*
[b] *Biological Sciences Group, Birla Institute of Technology and Science, Pilani 333031, Rajasthan, India*
[c] *School of Physics, University of Hyderabad, Hyderabad 500046, AP, India*

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ABSTRACT

Effect of viscosity and temperature on twisted intramolecular charge transfer (TICT) fluorescence of *trans*-2-[4-(dimethylamino)styryl]benzothiazole (DMASBT) have been studied. TICT fluorescence quantum yield in glycerol solution is found to be ~23-fold greater than that in ethylacetate as a non-viscous solvent. For high-viscosity solvent, the fluorescence quantum yield increases at low temperature due to the decrease in free-volume of the solvent, which favors the decrease in torsional relaxation of the molecule that induces the radiationless decay. However, the free-volume concept is not meaningful at a temperature much above the glass transition temperature when the free-volume is highly abundant. The temperature-dependent phenomenon provides a more accurate description compared to the viscosity-dependent study in a series of solvents of varying viscosity at a given temperature. The stabilization of the TICT state, as a consequence of the restricted motion of the $-N(CH_3)_2$ group in DMASBT, results in a large Stokes shifted fluorescence band. The TICT fluorescence characteristics of DMASBT are found to be different from that of molecular rotors. In solvents of low polarity, where TICT is practically zero, the molecule exhibits excited state temperature-induced *cis–trans* isomerization showing fluorescence emissions from both the isomers. However, temperature-induced TICT fluorescence quenching is observed in polar viscous medium without any isomerization. Results indicate that DMASBT can be a potential microsensor for biomimicking as well as real biological systems.



## 1. Introduction

Multichromophoric molecules displaying characteristic features of charge separation are well-suited model systems demonstrating charge transfer [1,2]. These molecules having intramolecular charge transfer (ICT) and twisted intramolecular charge transfer (TICT) characteristics show highly Stokes shifted fluorescence bands that depend on the chemical and physical properties of the medium [3]. Highly Stokes shifted fluorescence that appears in addition to the normal fluorescence as a result of twisting of the donor part around the single bond connector in a donor–acceptor system is called twisted intramolecular charge transfer (TICT) fluorescence as first suggested by Grabowski et al. [3].

Effect of viscosity and temperature on TICT fluorescence has been an interesting subject of research from long before [2,4]. There are recent reports on effect of solvent polarity and viscosity on TICT properties of various molecular systems such as coumarins, *N*,*N*′-dimethylaminobenzonitrile (DMABN), a group of molecules called fluorescent molecular rotors [4], 9-(*N*,*N*-dimethylamino)anthracene (9-DMA) [5], etc. Although solvent polarity causes a bathochromic shift of the emission band in all these compounds, this shift is smallest in the case of molecular rotors. Peak intensity is influenced strongly by solvent viscosity in DMABN and the molecular rotors, but polarity and viscosity influences cannot be separated with DMABN [4]. Coumarins, on the other hand are not sensitive to viscosity. The dependence of TICT fluorescence on viscosity of the medium has been widely reported and is thought to occur by a time-dependent intramolecular reorientation process [2,6,7]. Dey and Warner [5] have noticed strong dependence of fluorescence peak intensity of 9-DMA on solvent polarity and viscosity similar to DMABN. Mielniczak et al. [2] have studied on a solvent viscosity and polarity sensitive fluorescent

* Corresponding authors. Tel.: +91 1596 245073x238; fax: +91 1596 244183.
*E-mail addresses:* sksaha@bits-pilani.ac.in (S.K. Saha), ppurkayastha@bits-pilani.ac.in (P. Purkayastha).

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sensor, 4-(4-dimethylaminostyryl)pyridinium (DMASP) derivative. They explain that the enhancement of the TICT fluorescence intensity with the increase in the viscosity of the medium surrounding the fluorophores is due to the reduction of the non-radiative transitions induced by intramolecular reorientation and diffusional collisions with the solvent molecules and justified by the Debye–Stokes–Einstein (DSE) hydrodynamic model [7]. Haidekker et al. [4] have explained the dependency of the emission intensity of molecular rotors by studying viscosity-dependent phenomena in the solvent of varying viscosities at a constant temperature through a power law relation proposed by Förster and Hoffmann [8] suggesting that the relaxation process is much deviated from the DSE diffusion in the high-viscosity region. In the present work on DMASBT it has been observed that although DMASBT is structurally similar to DMASP but the relaxation process is dependent on the temperature- and viscosity-dependent free-volume of the solvent proposed by Loutfy and Arnold [7] rather than the DSE hydrodynamic model. Moreover, temperature-dependent phenomena provides better description of the torsional relaxation rather than viscosity-dependent study at a constant temperature which is in contrary to the study on some molecular rotors by Haidekker et al. [4]. The free-volume concept [7] rather than the DSE hydrodynamic model gives more satisfactory result to explain the high quantum yield in the highly viscous solvents at low temperature. Recently, Dey and Warner [5] have ruled out the association of large Stokes shifted fluorescence with the TICT process in the viscous medium without any specific reason. But this work suggests that TICT fluorescence can be highly Stokes shifted in viscous medium and the probable reason for the same has been discussed. It has also been observed in this study that not only the fluorescence quantum yield of DMASBT is dependent on viscosity but also the fluorescence band is highly red shifted in a polar solvent [9], which is in contrary to the molecular rotors. The present report on DMASBT shows that unlike coumarins and molecular rotors, both solvent polarity and viscosity have their own effects on emission intensity as well as on emission wavelength. It has been demonstrated that in case of DMASBT this effect is not as complex as DMABN [4]. It can be mentioned that many cellular and organismal functions are related to the viscosity of their environment, and the alteration in cell membrane viscosity is well known to be responsible for several diseases, e.g. cell malignancy, hypercholesterolemia, atherosclerosis and diabetes [4].

In view of the development of a method that could be applicable for the measurements of viscosity in biological systems, and in particular real-time measurements of viscosity changes on a microscopic scale, the present study aims to get a fluorescent molecule that can act as a microsensor for biomimicking as well as real biological systems. We chose DMASBT because of high sensitivity of its fluorescence properties on polarity and pH [9] of the environment. The present work is mainly focused on to see the sensitivity of TICT fluorescence of DMASBT on the viscosity of the medium. Although, some success to measure the viscosity in biological systems has been accomplished through the use of molecular rotors by means of their viscosity-dependent fluorescence quantum yields, but the micropolarity of the biological systems can also get changed due to the intercalation of water molecules. The molecular rotors cannot sense this too effectively. It is also worth mentioning here that conventional mechanical viscometers are cumbersome to use and are incapable to perform real-time viscosity measurements.

Another important excited state process is photoisomerization. A system of excited state charge transfer coupled with isomerization under a certain condition can be an interesting model for important natural photoprocesses like photosynthesis and vision. It is now quite well known that the molecular properties get changed remarkably on photoisomerization [10–15]. In the present work, temperature-dependent excited state isomerization process has also been studied to see how excited state isomerization affects the charge transfer phenomenon. DMASBT has been reported to have non-genotoxicity [16].

## 2. Experimental

### 2.1. Materials and methods

DMASBT was procured from Aldrich Chemical Company, WI, USA. The methods of recrystallization and purity check are mentioned elsewhere [9]. All the solvents used are of spectroscopic grade and procured from Spectrochem Chemical Company, India. Triple distilled water was used for the preparation of the aqueous solutions. To record the UV–vis absorption and fluorescence spectra of DMASBT in pure solvents, a stock solution of DMASBT ($1.001 \times 10^{-3}$ M) was prepared in pure methanol, 0.1 mL of which was poured in a 10 mL volumetric flask and left for a few hours for complete evaporation of methanol and then the compound was dissolved in respective solvents to make the final volume to 10 mL. For the preparation of solutions in different percentages of the glycerol–water mixtures, 0.05 mL ($2.002 \times 10^{-3}$ M) of DMASBT solution in methanol was added to a mixture of glycerol and water and the final volume of it was adjusted to 10 mL. Methanol was added due to low solubility of DMASBT in water as well as glycerol–water mixture. The percentage of methanol present in glycerol–water mixture is only 0.5. The concentration of DMASBT in all the experimental solutions used for spectroscopic measurements was $1.001 \times 10^{-5}$ M. The fluorescence quantum yields were determined with respect to that of quinine sulfate in 0.1N $H_2SO_4$ as 0.55.

The absorption spectra were recorded using a Jasco V570 UV–vis spectrophotometer. Fluorescence measurements were performed using a Shimadzu RF-5301PC scanning spectrofluorimeter. Fluorescence lifetimes were determined from time-resolved intensity decay by the method of time-correlated single-photon counting using a picosecond diode laser at 370 nm (IBH, U.K., nanoLED-07) as light source. The typical response time of this laser system was 50 ps. The fluorescence decays were deconvoluted using IBH DAS6 software. Mean (average) fluorescence lifetimes for biexponential iterative fittings were calculated from the pre-exponential factors and the decay times using the following equation [17]:

$$< \tau >= a_1\tau_1 + a_2\tau_2 \quad (1)$$

The steady-state fluorescence anisotropy measurements were performed with the same steady state spectrofluorimeter fitted with a polarizer attachment. The excitation and emission bandwidths used for the anisotropy measurements were 5 nm each. The steady state anisotropy, $r$ can be represented as [18]

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}} \quad (2)$$

where $I_{VH}$ and $I_{VV}$ are the intensities obtained from the excitation polarizer oriented vertically and the emission polarizer oriented in horizontal and vertical positions, respectively. The factor $G$ is defined as

$$G = \frac{I_{HV}}{I_{HH}} \quad (3)$$

where $I$ terms refer to parameters same as mentioned above for the horizontal position of the excitation polarizer. All measurements other than the study of temperature effect were done at room temperature (25 °C).

To study the temperature dependence of the fluorescence of DMASBT, a simple on–off temperature controller was designed. A suitable heater made of aluminium block was fabricated for holding