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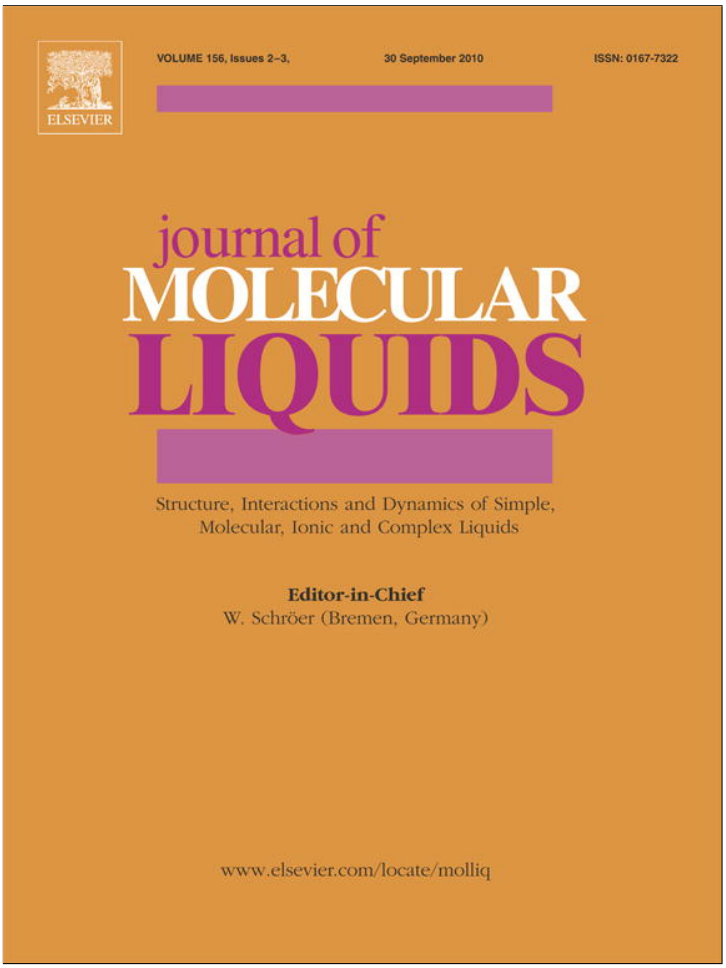

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Intramolecular charge transfer promoted fluorescence transfer: A demonstration of re-absorption of the donor fluorescence by the acceptor

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ABSTRACT

Intramolecular charge transfer (ICT) promoted fluorescence transfer has been investigated in two polar solvents, acetonitrile and water. The ICT species of 4-N,N-dimethylaminobenzonitrile (DMABN) produced exclusively in the photoexcited state serves as the donor while phenosafranin (PSF), a cationic phenazinium dye, acts as the acceptor. A transfer of the fluorescence occurs from the ICT state of DMABN to PSF in both the media. Time-resolved fluorescence decay analysis in combination with the steady state fluorometric observations conclusively rule out the involvement of the fluorescence resonance energy transfer (FRET) process and establish the fluorescence transfer as a consequence of re-absorption of the fluorescence of the donor by the acceptor. Thus, apart from citing an example of a coupled interaction of ICT and fluorescence transfer, importance of the present work lies in providing a demonstration in differentiating between the Förster resonance energy transfer and the trivial energy transfer through re-absorption.

1. Introduction

The photoinduced intramolecular charge transfer (ICT) is the basis function for many photoelectronic devices [1] as well as is the basic mechanism for biological and chemical energy conversions [2–4]. This photoinduced ICT of organic molecules containing an electron-donor and an electron-acceptor group has been an exciting topic in modern photoresearch. Since the initial investigation of the dual fluorescence of 4-N,N-dimethylaminobenzonitrile (DMABN) by Lippert et al. [5] and the introduction of the concept of twisted intramolecular charge transfer (TICT) by Grabowski et al. [6], the spectral studies of such typical donor–acceptor charge-transfer molecules, have been fascinating to researchers both from the fundamental and application points of view [7]. In ICT molecules, an electron donor unit and an electron acceptor unit are often coupled through a motif of alternating single and double bonds. After absorption of the photon, the intramolecular charge delocalization takes place in the excited state which is manifested in the fluorescence characteristics of the probe in solvents of different polarity.

A well-explored example of an ICT probe is DMABN [6]. The solvent dependent dual fluorescence of DMABN, first observed by Lippert et al., has been thoroughly explored both experimentally and theoretically [5,8]. The dual fluorescence which is an apparent violation of Kasha's rule has been explained in terms of a reversible charge transfer reaction between a locally excited state (LE) and an intramolecular charge transfer (ICT) state that is stabilized in polar solvents [5,8]. Several researchers have concentrated on the structural change that accompanies the ICT process [9–13]. Among the various proposed models the monomolecular TICT model is mostly favored [9–13], in which the dimethylamino group lies in the plane of the phenyl ring in the LE state and twists to an approximately perpendicular configuration in the ICT state. Upon photoexcitation in the UV region in suitable polar solvent, DMABN shows fluorescence from both the locally excited (LE) as well as the charge transfer (CT) states. The higher energy, less solvent dependent emission band is assigned to the emission from a benzenoid type $\pi\pi^*$ LE state and the lower energy, highly solvent-sensitive emission band to that from a highly polar ICT state [6]. The role of the solvent has been one of the controversial issues. Its crucial importance in stabilizing the ICT state of DMABN is demonstrated by the absence of the low energy fluorescence from this molecule in the gas phase [14,15]. A two-state equilibrium model (LE $\rightleftharpoons$ ICT) with polarity dependent activation energy is adequate to describe the behavior in polar aprotic solvents [16–18]. However, the results in polar protic solvents are complex and often appear to be seemingly contradictory when analyzed in the same way [16].

Another significant photoprocess in the league is the energy transfer process. The energy transfer process can be of three categories in terms of the mechanism it follows: Dexter transfer, Förster transfer and radiative or trivial energy transfer *via.* re-absorption. In Dexter transfer, the transfer of the excitation energy occurs non-radiatively through electron exchange mechanism for short distances typically in the range 15–20 Å [19]. This energy transfer process requires diffusion of excitons from the donor to the acceptor following Wigner–Witmer spin conservation rules [20]. The second nonradiative energy transfer is the

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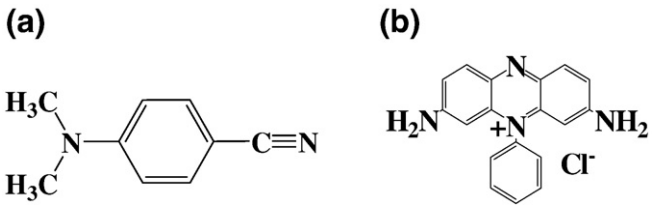
fluorescence or Förster resonance energy transfer (FRET) where the excitation energy of a donor is transferred to a nearby acceptor molecule *via.* a through-space dipole–dipole interaction between the donor–acceptor pair [19,21–25]. The donor–acceptor distance is in the range 20–90 Å for the Förster transfer to be effective [19]. Resonance energy transfer can yield a significant amount of structural information concerning the donor–acceptor pair and that is why fluorescent organic molecules have been widely used as energy donors and/or acceptors in a variety of FRET-based biological studies [19,26,27]. The ability of FRET in measuring the intermolecular as well as intramolecular distances makes it a "spectroscopic ruler". In contrast to the non-radiative energy transfer processes, the radiative energy transfer occurs through the transfer of excitation energy by radiative deactivation of a donor molecule followed by the re-absorption of the emitted radiation by an acceptor molecular entity [19]. In essence there is no actual interaction between the donor and the acceptor. This type of energy transfer depends upon the non-molecular optical properties of the sample such as the intensity of the excitation source, optical path length and optical density of the sample at the excitation wavelength etc. [19]. This trivial energy transfer does not give any meaningful information regarding the structural aspect of the interacting partners. In both the FRET and the re-absorption processes a reduction in the fluorescence of the donor molecular system is observed with the addition of the acceptor. Hence, there are chances of confusion about the occurrence of the FRET or the re-absorption phenomenon since in both the cases the steady state fluorometric observations resemble to a good extent. The steady state observations often do not leave an indication to pin-point which of the two processes is actually taking place. However, these processes can be well distinguished from the fact that in the case of Förster energy transfer, the fluorescence quantum yield and fluorescence lifetime of donor decreases parallely in the presence of the acceptor, while for the re-absorption process the fluorescence lifetime of the same remains unchanged.

Paying attention to the observation of the dual fluorescence of DMABN in various polar solvents, we have endeavored to couple the two photoprocesses namely, ICT and the fluorescence transfer. It has been found that fluorescence transfer occurs from the ICT probe DMABN to a potentially bioactive cationic phenazinium dye, phenosafranin (PSF) where the ICT species of DMABN produced exclusively in the photoexcited state serves as the donor. Considering the fact that the dye absorbs mostly at a region where the photoproduced ICT species of DMABN emits, i.e., a good overlap of the emission of the ICT band of DMABN and the absorbance of the acceptor (PSF) exists, the fluorophores are judged to be a compatible pair for the ICT promoted fluorescence transfer phenomenon. It is known that with an increase in the solvent polarity, the LE emission intensity of DMABN is reduced with a concomitant relative increase in the ICT fluorescence intensity [28–30]. For the present study we have chosen two solvents, water and acetonitrile, to see the effect of polarity of the solvent on the ICT triggered fluorescence transfer process. Phenosafranin (PSF, 3,7-diamino-5-phenyl phenazinium chloride) is a cationic dye of the phenazinium group (Scheme 1). The dye has been extensively used for various photophysical and photobiological applications as described elsewhere [31–36]. It is red in color with a planar tricyclic phenazinium moiety bearing a positive charge. With the coupled process in hand, we further endeavored to explore the mode of fluorescence transfer from the donor (DMABN) to the acceptor (PSF).



Scheme 1. Structures of (a) DMABN and (b) PSF.

In a couple of recent articles, similar studies have been made by our group [37,38] where excited state proton transfer (ESPT) promoted energy transfer has been explored. The works demonstrated that the pH of the medium regulates the efficiency of the energy transfer process. ESPT promoted fluorescence transfer thus has the potential to serve as sensor for the pH of solutions. In a similar fashion, the present work demonstrates an efficient solvent-sensitive fluorescence transfer from DMABN to PSF. The impact of the work lies in its exploitation in monitoring the polarity of the solvent. The other aspect of the work remains in distinguishing between FRET and the trivial energy transfer *via.* re-absorption. The ICT process being coupled to the fluorescence transfer to the acceptor, the LE ⇌ ICT equilibrium is supposed to be affected if the energy transfer proceeds through an interaction between the acceptor molecule and the photoproduced ICT species in its excited state. This should, in its turn, leave a signature on the LE fluorescence. On the other hand absence of such a signature should refer the energy transfer process to proceed through the re-absorption of the fluorescence of the ICT species by the acceptor molecule. Thus, the present coupled process is supposed to provide a better visibility into the intricate process.

2. Materials and methods

4-N,N-dimethylaminobenzonitrile (DMABN) and phenosafranin (PSF) were purchased from Fluka (USA) and Sigma-Aldrich (USA) respectively. The fluorophores were used as received. The purity of the compounds was checked from their respective absorption and emission spectra in standard solvents. Acetonitrile used was of UV-spectroscopic grade with >99.9% purity (Spectrochem, India). The concentration of DMABN was kept 6×10^{-5} M throughout the experiment in both aqueous and acetonitrile media. Triply distilled water was used to make the experimental solutions for the studies in aqueous medium.

Room temperature optical absorption and steady state fluorescence measurements were performed using a Shimadzu UV-2450 spectrophotometer and a Spex fluorolog-2 spectrofluorimeter equipped with DM3000F software respectively. The fluorescence lifetimes were determined from time resolved intensity decays by the method of time correlated single photon counting (TCSPC) using a nanosecond diode at 295 nm (IBH, UK, nanoLED-17) as the light source and TBX-04 as the detector. The instrument response time for the set-up was ~1 ns. The decays were analyzed using IBH DAS-6 decay analysis software. Goodness of the fits was evaluated from the χ^2 criterion and the randomness of the residuals.

The fluorescence spectra were resolved into overlapping Gaussian curves using MS Origin 7.0 fitting algorithm to obtain the minimum number of reproducible components using the adjustable parameters like center and width for the resolved bands. Multiple attempts to fit the data with different initial parameters generally provided a survey of the extent of statistically equivalent parameter sets. Comparing several resolutions of an overall spectrum, a "good fit" was judged from several criteria including a minimum in the goodness fit parameter χ^2 and the superposition of the convoluted curves on the experimentally obtained spectra [34,35,37]. From the statistically acceptable fits, a good fit was further judged by the reproducibility in the values of the centers of the Gaussian curves. A final, *albeit subjective*, criterion was to examine the fits for physically plausible results.

3. Results and discussion

3.1. Steady state studies

In aqueous medium DMABN gives a broad and unstructured low energy absorption band with maximum at around 296 nm. Upon

photoexcitation, DMABN gives two fluorescence bands: the higher energy one corresponding to the locally excited (LE) state and the lower energy one to the ICT state. The LE band ~365 nm is very feeble in intensity while the ICT band is observed prominent with a maximum at ~525 nm. The quantum yields of both the emissions are, however, quite low due to the high rate of ICT formation and efficient and fast non-radiative transitions to ground state and/or lower triplet states [28,39]. In acetonitrile a hypsochromic shift is observed in the ICT emission band. Also the LE band is noticeable. The LE band maximum appears at ~360 nm while the ICT state appears at ~480 nm. Consistent with the literature, observation of a more prominent LE band of DMABN in acetonitrile medium compared to that in water is ascribed to the fact that acetonitrile is less polar than water [5,8,28,39].

The absorption spectrum of PSF in aqueous solution shows a broad unstructured band with absorption maximum at around ~520 nm while the fluorescence spectrum gives a broad emission band at ~585 nm [31]. In acetonitrile, the absorption maximum of PSF is slightly blue shifted from that in water medium and peaks at ~517 nm. The emission maximum shows a marked blue shift and moves to ~560 nm. However, in both water and acetonitrile media, an appreciable overlap exists between the fluorescence band of the photoproduced ICT species of DMABN and the absorption band of PSF making them a matched pair for efficient ICT-promoted fluorescence transfer process.

On exciting the DMABN solutions (6×10^{-5} M) in both the solvents, gradual addition of PSF leads to a decrease in the fluorescence intensity of the ICT band of DMABN with a concomitant development of new emission bands at ~585 nm in water and ~560 nm in acetonitrile, corresponding to the emission of PSF in the two solvents respectively. The fluorometric observations in these two solvents are depicted in Fig. 1(a). Isoemissive points were observed at 553 nm and 535 nm in aqueous and in acetonitrile media respectively, which results from the fluorescence of the two distinct species namely, the ICT species of DMABN and the PSF.

In order to verify whether the fluorescence of PSF originates from the fluorescence transfer from DMABN or from the direct excitation, a blank experiment was performed with a given concentration of PSF in the absence of the donor. PSF was excited at 310 nm, where the donor had been excited. Insignificant fluorescence was observed from the fluorophore ruling out the direct excitation of PSF when both DMABN and PSF were present in the solution. Formation of any ground state complex is ruled out from the absorption and the excitation spectral observations where no new bands were noticed. Absence of any additional band in the fluorescence spectrum of the mixture of the donor and the acceptor (Fig. 1) rules out the possibility of the formation of any exciplex between the donor and the acceptor moieties.

Since in both aqueous and acetonitrile media a significant overlap was noticed between the ICT emission bands of DMABN and PSF, resolution of the spectra was necessary to get the individual contributions from the individual partners. The resolution was done in the frequency space since spectral band shape is better defined in the energy space. In the absence of the acceptor, the fluorescence spectrum of DMABN yielded two bands corresponding to the LE state (~365 nm in water, ~360 nm in acetonitrile) and the ICT state (~525 nm in water, ~480 nm in acetonitrile). On gradual addition of PSF, diminution of the fluorescence intensity of the band assigned to the ICT state of DMABN was observed along with a concomitant increase in the intensity of the new band corresponding to the emission of PSF. The overall fluorescence spectra obtained for different concentrations of the added PSF were resolved to get the contribution of the individual emission bands to the total fluorescence. This helped us to determine the extent of quenching of the donor fluorescence in the presence of PSF; thereby helping us in assessing the mechanistic detail of the energy transfer process.

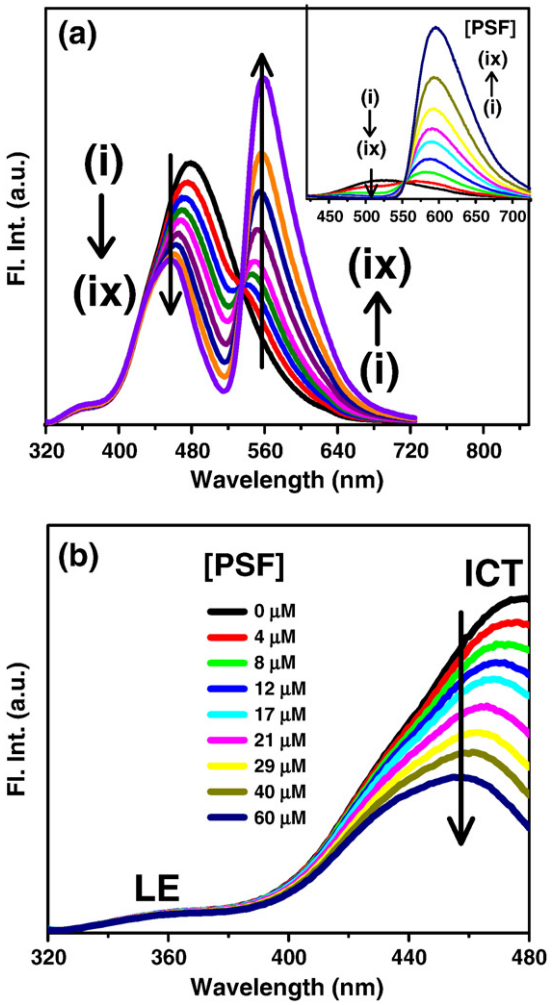


Fig. 1. (a) Fluorescence spectral variation of 6×10^{-5} M DMABN with the addition of PSF in acetonitrile. PSF concentrations in curves (i)→(ix) are 0, 4, 8, 12, 17, 21, 29, 40 and 60 μM respectively. $\lambda_{exc}=310$ nm. Inset shows a similar variation in water medium; PSF concentrations in (i)→(ix) being 0, 12, 30, 60, 90, 120, 150, 180 and 240 μM respectively. (b) Spectral variation in acetonitrile in the range 320 nm–480 nm in a magnified form to emphasize the relative change of the LE and the ICT bands. $\lambda_{exc}=310$ nm.

Sample resolved spectra in water and acetonitrile media are shown in Figs. 2 and 3 respectively.

Steady state emission studies reveal fluorescence quenching of the ICT band of DMABN (donor) in aqueous and in acetonitrile media with the gradual addition of PSF (acceptor). The fluorescence quenching is governed by Stern–Volmer equation as revealed from the linearity of the corresponding plots (Fig. 4).

$$F_0 / F = 1 + K_{SV}[Q] \quad (1)$$

$$K_{SV} = k_q.\tau_0 \quad (2)$$

where F_0 and F are the fluorescence intensities in the absence and the presence of the quencher respectively; K_{SV}, the Stern–Volmer quenching constant; k_q, the bimolecular quenching constant and τ_0, the lifetime of the fluorophore in the absence of the quencher [19]. The fluorescence was monitored at the emission maximum of the ICT band of DMABN. Slopes of the plots gave the K_{SV} values that came out to be 6.0×10^4 M^{-1} in water and 2.1×10^4 M^{-1} in acetonitrile. The k_q values are 6.0×10^{13} M^{-1} s^{-1} and 7.0×10^{12} M^{-1} s^{-1} in water and in acetonitrile respectively [τ_0 of ICT fluorescence of DMABN was determined to be 1.0 and 3.1 ns respectively in the two media]. The

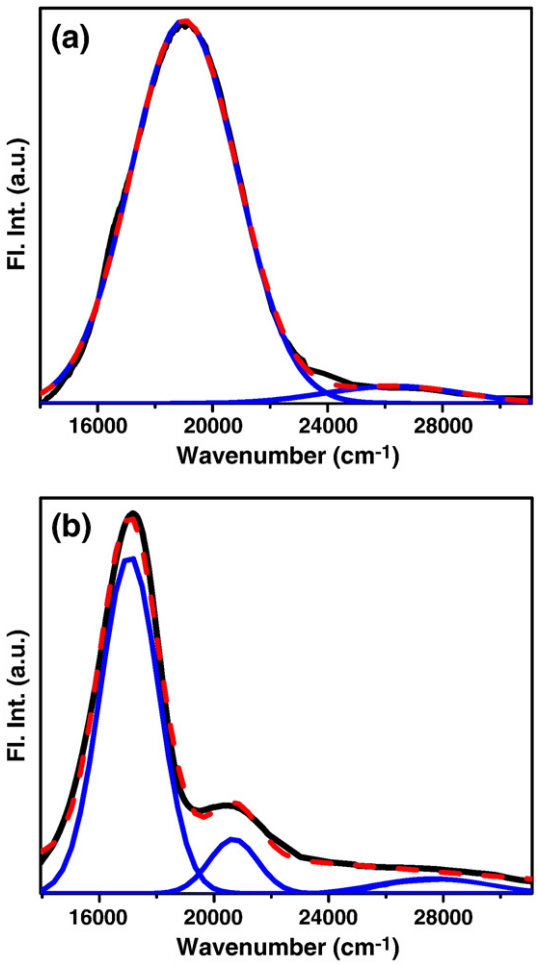


Fig. 2. Resolved fluorescence emission spectra in aqueous medium. Concentrations of PSF in (a) and (b) are 0 and 3×10^{-5} M. [DMABN] = 6×10^{-5} M. Black lines denote the experimental spectra, blue lines the resolved spectra and red dashed lines the convoluted spectra from the resolved bands.

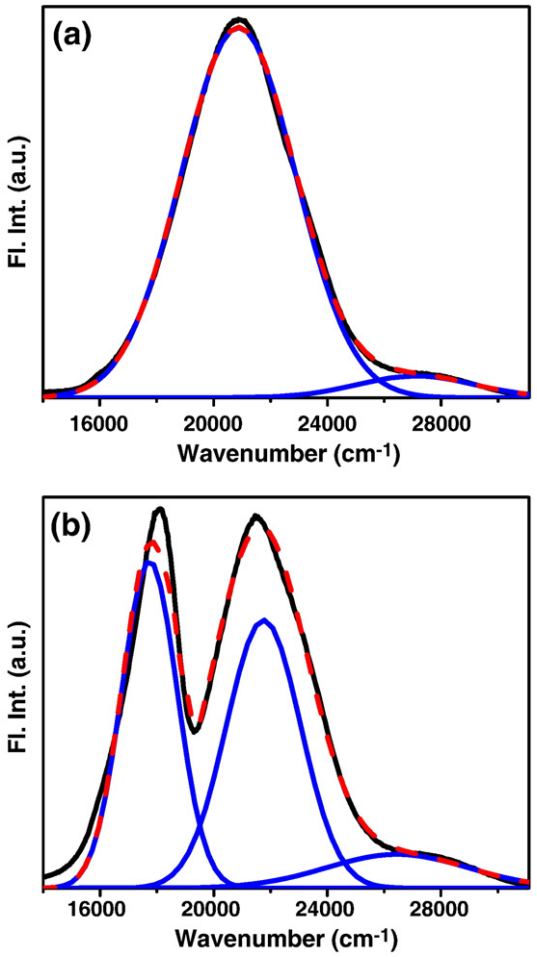


Fig. 3. Resolved fluorescence emission spectra in acetonitrile. Concentrations of PSF in (a) and (b) are 0 and 2.1×10^{-5} M respectively. [DMABN] = 6×10^{-5} M. Black lines denote the experimental spectra, blue lines the resolved spectra and red dashed lines the convoluted spectra from the resolved bands.

high value of k_q in both the solvents imply that the fluorescence quenching does not occur through diffusional collision between the two interacting partners and leaves the options that the excitation of PSF may occur either through Förster energy transfer from the ICT species of DMABN or through the trivial re-absorption of the ICT fluorescence by the PSF.

The essential criterion for both these processes, either through FRET or through re-absorption, is a significant overlap between the fluorescence spectrum of the donor and the absorption spectrum of the acceptor. The overlaps of the spectra in both the media are depicted in Fig. 5 to help the general readers to obtain an idea about the overlap of the emission band of the donor (the ICT species of DMABN) with the absorption band of the acceptor (PSF).

The steady state fluorometric observations thus indicate a fluorescence transfer from the photoproduced ICT species of DMABN to the ground state PSF. In order to understand the intricate mechanism we assess the following points critically. Although the steady state observations do not provide any confirmatory signal to discriminate between the two mechanistic pathways, they, of course, give some indications.

Firstly, had it been through FRET, the photoproduced ICT state of DMABN would have been decayed faster in the presence of the added acceptor (PSF) because of the introduction of a leakage channel, so to say, namely FRET. This is expected to shift the DMABN (LE) ⇌ DMABN (ICT) equilibrium more towards right resulting in a reduction (quenching) in the fluorescence intensity of the LE band along with the quenching of the ICT band. The steady-state fluorometric observations, however, indicate that the intensity of the LE fluorescence remains invariant, within the experimental limit, with the addition of PSF. The modification in the fluorescence intensities of the LE and the ICT bands of DMABN in acetonitrile with the addition of PSF is portrayed in Fig. 1(b). The figure confirms that the LE state bears no signature of quenching. Constancy of the intensity of the LE fluorescence, thus, suggests non-occurrence of the FRET in the present case and indicates re-absorption of the ICT fluorescence by PSF followed by its own emission. The LE band in water being imperceptible it is difficult to look for such a change in aqueous medium.

Secondly, Fig. 1(a) shows a gradual blue shift in the donor fluorescence (ICT of DMABN) with an increasing acceptor concentration. This is not expected had the Förster energy transfer been involved. The positions of the emission maximum of the ICT band and that of PSF being defined in a specific solvent, occurrence of FRET should lead only to the diminution of the ICT band with a concurrent development of the PSF emission. Neither emission is expected to show any shift in their band positions with the gradual addition of PSF. The gradual blue shift in the ICT emission with added PSF, thus, indicates that the energy transfer proceeds not through FRET but through re-absorption. For a re-absorption process such a shift is expected since with an increase in the acceptor concentration it will

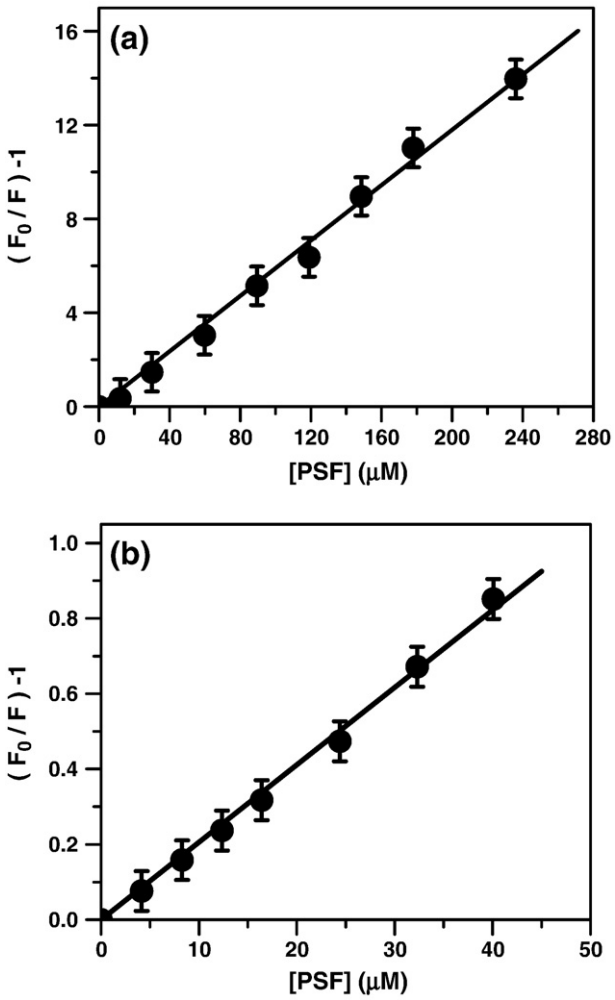


Fig. 4. Stern Volmer plot for the quenching of fluorescence of the ICT band of DMABN by PSF in (a) aqueous and (b) acetonitrile media.

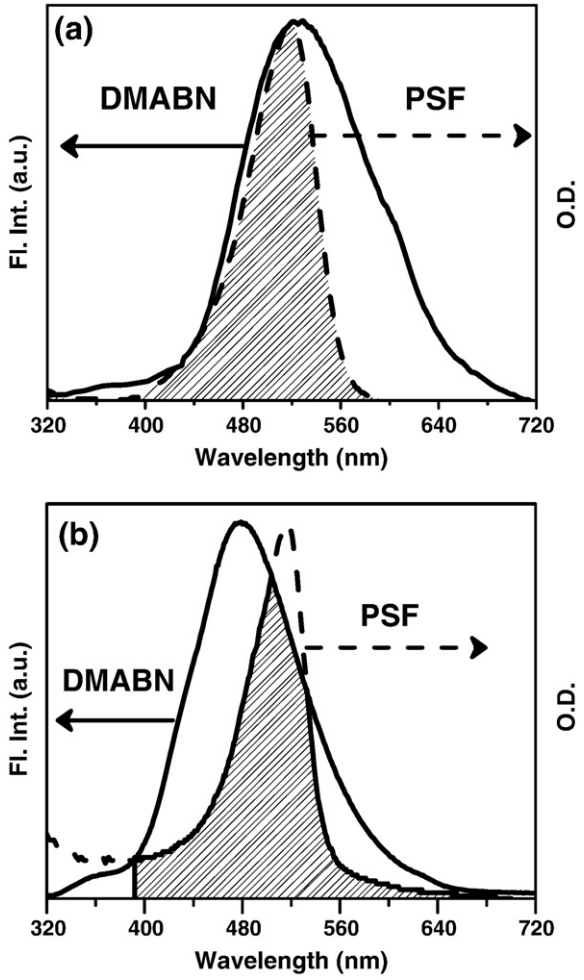


Fig. 5. Overlaps between the emission spectrum of the ICT band of DMABN (donor) and the absorption spectrum of PSF (acceptor) in (a) water and (b) acetonitrile media.

absorb more. In acetonitrile, the absorption maximum of PSF being in the red range (~517 nm) of the band maximum of the ICT emission (~480 nm), a greater amount of absorption by the added acceptor would result in a visual blue shift in the ICT peak position — consistent with the steady state findings.

The conclusive evidence to resolve the problem, however, comes from the time-resolved fluorometric study as described below.

3.2. Time-resolved study

The fluorescence lifetimes of both DMABN and PSF have been monitored in both the solvents (water and acetonitrile). In water, the individual lifetimes of both the ICT emission of DMABN (monitored at 525 nm) and the PSF emission (monitored at 580 nm) have been found to be ~1 ns. However, in acetonitrile the lifetime of the ICT emission (monitored at 450 nm) is determined to be 3.08 ± 0.3 ns and that of the PSF emission (monitored at 580 nm) is 3.5 ± 0.3 ns. All these lifetime data comply with the literature values [40–42].

The fluorescence lifetime of the ICT state of DMABN is found to remain the same in the absence as well as in the presence of the added acceptor (Fig. 6), although the steady state fluorescence spectra revealed a gradual quenching of the donor fluorescence with the addition of PSF. The lifetime data in acetonitrile medium are presented in Table 1. Constancy in the fluorescence lifetime of the donor (ICT) emission in the absence and in the presence of varying amount of the added acceptor (PSF) affirms that the fluorescence quenching proceeds through a static process and conclusively rules out the occurrence of FRET in the present case. The fluorescence of PSF is, thus, ascribed to originate from the re-absorption of the ICT fluorescence of DMABN by the added PSF.

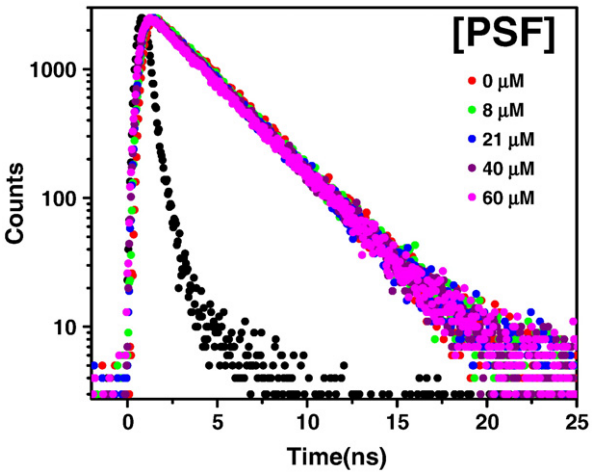


Fig. 6. Time-resolved fluorescence intensity decays of the ICT band of DMABN ($\lambda_{exc} = 295$ nm and $\lambda_{em} = 450$ nm) in acetonitrile and in varying concentrations of PSF. The concentrations of PSF are provided in the legends. The sharp profile in black is the instrument response function.

Table 1
Fluorescence decay times of the ICT band of DMABN ($\lambda_{exc} = 295$ nm and $\lambda_{em} = 450$ nm) in the presence of varying concentrations of PSF.

[PSF] (μM)	τ (ns)	χ^2
0	3.10 ± 0.3	1.2
8.0	3.08 ± 0.3	1.1
21.0	3.08 ± 0.3	1.2
40.0	3.08 ± 0.3	1.1
60.0	3.07 ± 0.3	1.0

4. Conclusions

An efficient fluorescence transfer has been envisaged from DMABN to PSF exclusively through photoinduced intramolecular charge transfer phenomenon. The photoproduced ICT state of DMABN serves as the donor while PSF as the acceptor. The pair demonstrates an efficient solvent polarity sensitive fluorescence transfer from the former to the latter. The present work resolves the problem in assessing the occurrence of the fluorescence transfer through re-absorption rather than through FRET. The steady state fluorescence quenching simply infers transfer of fluorescence from the donor to the acceptor but the exact mechanism remains undisclosed. A number of aspects have been suggested to decipher the mechanism, the time-resolved studies providing the confirmation. Constancy of the fluorescence lifetime of the donor (ICT of DMABN) in the absence and the presence of the added PSF affirms that the fluorescence transfer follows a re-absorption process and FRET is in no way involved into it. Since occurrence of the ICT process depends very much on the solvent polarity, a possible application of the present work lies in the determination of the micropolarity around the donor looking at the emission of the acceptor at a much longer wavelength (yellow to red region).

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