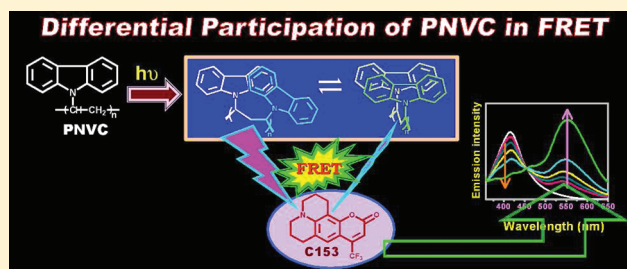


Differential Förster Resonance Energy Transfer from the Excimers of Poly(*N*-vinylcarbazole) to Coumarin 153

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ABSTRACT: Photophysics of the nonconjugated vinyl polymer poly(*N*-vinylcarbazole) (PNVC) has been explored in the presence of coumarin 153 (C153) exploiting steady state and time-resolved fluorometric techniques. Dual emission from the two distinct excimers of PNVC adds importance to the study and makes it interesting. The study substantiates the occurrence of Förster resonance energy transfer (FRET) from PNVC to C153. The differential involvement of the two excimers in the energy transfer process has been established. Considering the fact that FRET is a long distance dipole induced phenomenon, this differential effect has been rationalized from a difference in the dipole moments of the two excimers. Determination of the quenching constants reveals an order of magnitude more quenching of the high energy excimer than the low energy one in the presence of the quencher C153.



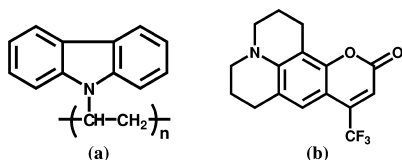
1. INTRODUCTION

The recognition of important processes such as energy migration and excimer formation and their role in determining the photochemical characteristics of the macromolecules has led to an enormous growth in the study of pendant polymer photophysics in recent years. The photophysical properties of the aromatic polymers are under the target of massive research for its diverse applications.^{1,2} The aromatic chromophores pendant to the polymer backbone serve as fluorescent labels.³ The chromophoric units may be appended to one end or to both the ends, or they may be distributed over the chain of the polymer in a regular fashion. The latter two situations often lead to the appearance of a broad structure-less emission assigned to an excimer that provides information about the structural and dynamical aspects of the polymer rather easily.^{4,5} In the present study, we have exploited a member of the third category pendant polymers, namely, poly(*N*-vinylcarbazole) (PNVC) (Scheme 1a), a nonconjugated vinyl polymer. Because of the dynamics of the flexible polymer chain, the vinyl polymers show characteristic photophysical and photochemical properties such as intramolecular excimer formation and

intrachain energy migration, reflecting a high local concentration of the chromophores.^{6,7}

With the advances in bioanalytical sciences, materials with properties like multiple emissions under single wavelength excitation derive considerable attention in multiplexed bioassay.⁸ Among the vinyl polymers, PNVC has been an attractive supramolecular organic semiconductor because of its characteristic photophysical and photochemical properties exhibiting dual emission in the blue-violet region attributed to the two configurationally different excimers formed from the π -stacking of the pendant chromophoric units.^{9–12} Although the diffusion mechanism is ascribed to be responsible for the formation of the excimer for small molecules in solutions,^{13,14} the mechanism in polymers is yet to be established. However, formation of the excimer results from the association of the two pendant chromophores, one of which is electronically excited.^{9–15} Since PNVC has pendant chromophores in high density along the polymer chain, intramolecular excimer formation dominates over the formation of the intermolecular excimer.¹⁶ Contrary to other pendant polymers exhibiting monomer-like fluorescence of the individual fluorescent units, the broad blue-violet emission of PNVC is attributed to the overlap of two distinct excimers of the carbazole moieties.^{17,18} The broad fluorescence of PNVC was first observed by Klöpffer in solution phase as well as in film.¹⁷ Existence of the two excimers of PNVC was later on established by Johnson¹⁰ and Itaya et al.¹¹ The explicit fluorometric characterization of the two excimers revealing the existence of an equilibrium between

Scheme 1. Structures of (a) Poly(*N*-vinylcarbazole) (PNVC) and (b) Coumarin 153 (C153)



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them in the photoexcited state has been reported by us only recently.¹⁸ The emission peaking at ~ 370 nm is attributed to the partially overlapped excimer involving only one eclipsed aromatic ring from each carbazole group. The excimeric species giving the lower energy emission peaking at ~ 420 nm is assigned to the fully overlapped excimer with a sandwich-like conformation.^{10,11,18} The configuration and the conformation of the excimer formed in bis(carbazoles) was thoroughly studied by De Schryver et al.^{7,19,20} Contrary to their observation of the emission from the isolated carbazole chromophore along with the emission from the intramolecular excimers formed from the probes (1,3-di-*N*-carbazolylpropane and rac- and meso-2,4-di(*N*-carbazolyl)pentane) in alkane solvents, steady state and time-resolved fluorometric studies reveal no indication of emission from the monomeric carbazole moiety in the PNVC system.

This interesting photophysics has stimulated extensive research on this semiconducting PNVC polymer in the field of electronics concentrating on manufacturing opto-electronic devices like solar cells, polymer field effect transistors (PFETs), polymeric light emitting diodes (PLEDs), etc. Owing to the good hole transport property attributed to the intrachain π - π stacking alignment, PNVC has been widely used in the fabrication of blue-light emitting diodes.^{12,21–25} PNVC also serves as an efficient donor material for energy transfer to many acceptor molecules.²² The semiconducting polymer systems often participate in the energy transfer process, and they are mostly comprised of polymer–polymer and polymer–dye blends, which leads to tunable colored emissions in display systems. The excitation energy transfer from the semiconducting polymers to fluorescent dyes or dye-labeled analytes is exploited in sensor applications like DNA and protein sensing.^{26,27} Recent reports on the amplified quenching of the fluorescent polymers by nanoparticles open up a new avenue for the development of polymer-based sensors.^{28–30}

Both radiative and nonradiative mechanisms have been invoked to analyze and explain the energy transfer (ET) in general.^{31–35} Radiative energy transfer involves the emission of a photon by the excited donor and subsequent reabsorption by the acceptor, resulting in the fluorescence of the latter.^{35,36} In essence, there is no direct interaction between the donor and the acceptor and hence the trivial energy transfer via reabsorption does not give any valuable information regarding the structural aspect of the interacting partners. Nonradiative energy transfer, also known as Förster resonance energy transfer (FRET), is a more efficient and rapid process.^{35–39} Here the electronic excitation energy of the donor chromophore is transferred to the nearby acceptor molecule via a through-space dipole–dipole interaction. The confirmatory test of FRET is the time-resolved fluorescence decay analysis and not the steady state quenching study.^{35,36} A reduction in the fluorescence lifetime of the donor with the gradual addition of the acceptor establishes the occurrence of FRET. The strong distance dependence (r^{-6}) of the efficiency of the process is the key for exploitation of FRET in studying the structure and dynamics of macromolecules and biomacromolecules. The ability to determine the intermolecular and intramolecular distances has coined the FRET process as a “spectroscopic ruler”.^{35,36,39} To expand the scope of energy transfer (ET), recently we have coupled other photoprocesses like excited state proton transfer (ESPT) and intramolecular charge transfer (ICT) with ET to promote newer paths to

bypass the circumstances where direct energy transfer from the donor to the acceptor is restricted.^{36,40,41}

Considering a good overlap between the fluorescence spectrum of PNVC (Scheme 1) and the absorption spectrum of the well studied fluorescent laser dye C153 (Scheme 1), the pair has been chosen for a possible energy transfer from PNVC to C153. Apart from being a prominent laser dye, coumarin has varied physiological activities such as anticoagulant, antibacterial, antihelminthic, etc.⁴² The solvent sensitive spectral behavior of the dye has made it popular for deciphering various aspects including solvation dynamics.^{43–47}

In the present work, we have studied the energy transfer from the nonconjugated polymer (PNVC) to the laser dye (C153). The primary objective of the work remains in deciphering the differential involvement of the two excimers in the energy transfer process.

2. EXPERIMENTAL SECTION

Poly(*N*-vinylcarbazole) is synthesized following the method described elsewhere.^{48,49} The molecular weight of PNVC homopolymer was determined viscometrically in toluene using the relation $[\eta]_{\text{PNVC}} = 7.62 \times 10^{-4} [M]^{0.5}$, where $[\eta]$ is the intrinsic viscosity and M is the molecular weight of the polymer. The average molecular weight of PNVC is determined to be 88000.^{49–51} Coumarin 153 purchased from Aldrich (USA) is used as received. Spectrophotometric grade toluene is procured from Aldrich (USA) and used without further purification. Triply distilled water is used to prepare the aqueous solutions wherever required. Solubility of PNVC in water being low, the aqueous solution of PNVC is prepared by sonication in ultrasonic cleaner followed by repeated filtration. Concentration of PNVC is kept at a low level ($\sim 2.0 \times 10^{-5}$ mol dm⁻³) in both toluene and water media to avoid any possible intermolecular effect.

Room temperature absorption and steady state fluorescence measurements are performed using a Shimadzu UV-2450 spectrophotometer and a Spex fluorolog-2 spectrofluorometer equipped with DM3000F software, respectively. Fluorescence lifetimes are determined from time-resolved intensity decays by the method of time-correlated single-photon counting (TCSPC) using nanosecond diode excitation sources at 295 and 403 nm (IBH, UK, nanoLED-17, nanoLED-07) and TBX-04 as the detector. The instrument response time is ~ 1 ns. The decays are deconvoluted using IBH DAS-6 decay analysis software. The quality of the fits is judged by the reduced χ^2 criterion and the randomness of the fitted function to the raw data. The biexponential decay profile is described by $I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$, where τ_1 and τ_2 are the decay times and a_1 and a_2 are their relative amplitudes. All the experiments are performed at ambient temperature (27 °C) with air-equilibrated solutions.

The ground state electronic structure based calculations on models of the PNVC dimers have been performed using the Gaussian 03 suite of the quantum chemical program.^{52,53} The geometry of the carbazole monomer is optimized using the MP2/6-31G* level of theory. Carbazole dimers are constructed from the optimized geometry of the monomer following the strategy of Claire allowing the relative orientation to change.⁵³ The planes containing the carbazole units are kept parallel with each other in the model. The energy minimized structures are obtained for an interplanar separation of ~ 3.5 Å.

3. RESULTS AND DISCUSSION

3.1. Steady State Studies. In both toluene and water, the lowest energy structured absorption band of PNVC spans 300–360 nm peaking at ~340 nm. The spectral pattern and the absorption maxima of the two bands do not change appreciably in the two solvents.¹⁸ Photoexcitation of PNVC at the low energy absorption band (340 nm) yields a broad fluorescence spectrum in both the solvents with two bands having band maxima at ~370 and ~415 nm. Consistent with the literature, the high energy emission band is assigned to the partially overlapped excimer while the lower energy one to the fully overlapped sandwich excimer.^{10,18,54–56} Resolution of the fluorescence spectra in toluene and water yields the individual bands corresponding to the two excimers. In toluene, the individual emission peaks come at 370 and 415 nm, respectively, and the corresponding peaks in water come at 380 and 416 nm.¹⁸ A greater red shift in the emission of the high energy emitting excimer than the low energy one with an increase in the solvent polarity indicates that the former is more polar than the latter (*vide infra*). As already stated, contrary to many other pendant polymers exhibiting excimer fluorescence, the striking feature of the emission spectra of PNVC is the absence of the structured emission band characteristic of the isolated carbazole units in both the solvents (Figure 1). This is ascribed to the high concentration of the pendant carbazole units facilitating formation of the excimers. It is pertinent to mention here that the nature of the emission spectrum of the polymer is independent of the excitation wavelength within the absorption band, thereby confirming that the ground state consists of a single species and formation of the excimers occurs purely in the photoexcited state.¹⁸

The absorption spectra of C153 in toluene and water media show broad unstructured bands with maxima at ~410 and ~430 nm, respectively (cf. Figure 7). Thus, in both media, there remains appreciable spectral overlap between the fluorescence of PNVC and the absorption of C153, making them a possible compatible pair for an energy transfer to occur. The broad fluorescence spectra of C153 appear with band maxima at ~480 and ~550 nm in the two solvents, respectively.⁵⁷

Addition of C153 leads to a gradual quenching of the PNVC fluorescence in both the solvents along with a concomitant development of the emission band corresponding to the acceptor dye. Figure 2 depicts the fluorometric observations in the two solvents. Observation of the isoemissive points (at 430 nm in toluene and at 455 nm in water) emphasizes that the energy transfer is confined exclusively between PNVC and C153. Blank experiments are conducted in both the solvents with C153 in the absence of PNVC, exciting the system at the polymer absorption (340 nm) as before. Imperceptible fluorescence observed under these conditions rules out the direct excitation of the acceptor and thereby points to the occurrence of the energy transfer process. Absence of any new band either in the absorption or in the emission spectra other than those of the polymer and C153 negates the formation of any complex between the interacting partners in either of the ground or the excited states.

Quenching of the fluorescence of the donor (PNVC) with the addition of the acceptor (C153) follows the Stern–Volmer relation

$$F_0/F = \tau_0/\tau = 1 + K_{SV}[Q] = 1 + k_Q\tau_0[Q] \quad (1)$$

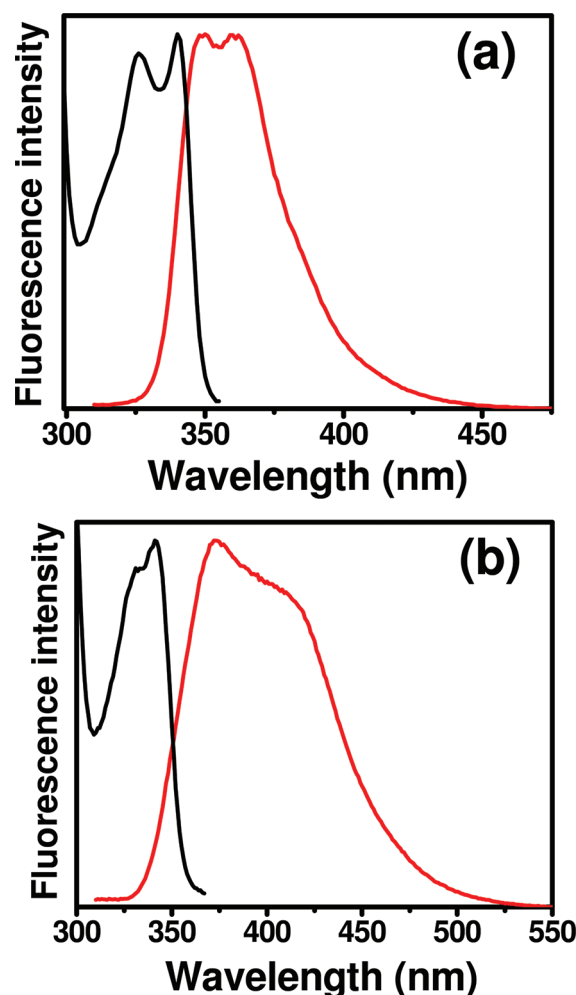


Figure 1. Normalized fluorescence (red) and fluorescence excitation (black) spectra of (a) NVC and (b) PNVC in toluene. For (a) $\lambda_{\text{exc}} = 300$ nm and $\lambda_{\text{em}} = 365$ nm and for (b) $\lambda_{\text{exc}} = 300$ nm and $\lambda_{\text{em}} = 440$ nm.

where F_0 and F are the fluorescence intensities of PNVC in the absence and presence of the quencher Q (C153), respectively, τ_0 and τ are the corresponding lifetimes, K_{SV} is the Stern–Volmer constant, and k_Q is the bimolecular quenching constant. To assign whether the energy transfer process is FRET or radiative reabsorption, it is important to assess whether the quenching is static or dynamic in nature. To resolve this, we move to the time-resolved fluorescence decay analysis which is the definitive way to differentiate between the two.^{35,36}

3.2. Time-Resolved Studies. The time-resolved fluorescence decays of the donor (PNVC) and the acceptor (C153) have been monitored in both toluene and water. On the basis of the available excitation source, for the time-resolved studies, the donor is excited at 295 nm and the emissions are monitored at 400 and 435 nm in toluene and water, respectively. In the absence of C153, PNVC shows biexponential decay profiles in both of the media. In toluene, the two lifetimes come as 2.5 ± 0.2 and 12.0 ± 0.4 ns. In water, the corresponding values are obtained as 6.86 ± 0.3 and 28.9 ± 0.5 ns. The lifetime values are consistent with the available literature data, the shorter-lived one (τ_1) corresponding to the high energy excimer while the longer-lived one (τ_2) to the low energy excimer of PNVC.^{18,58} The absence of fluorescence from the isolated carbazole monomer has also been confirmed from the time-resolved

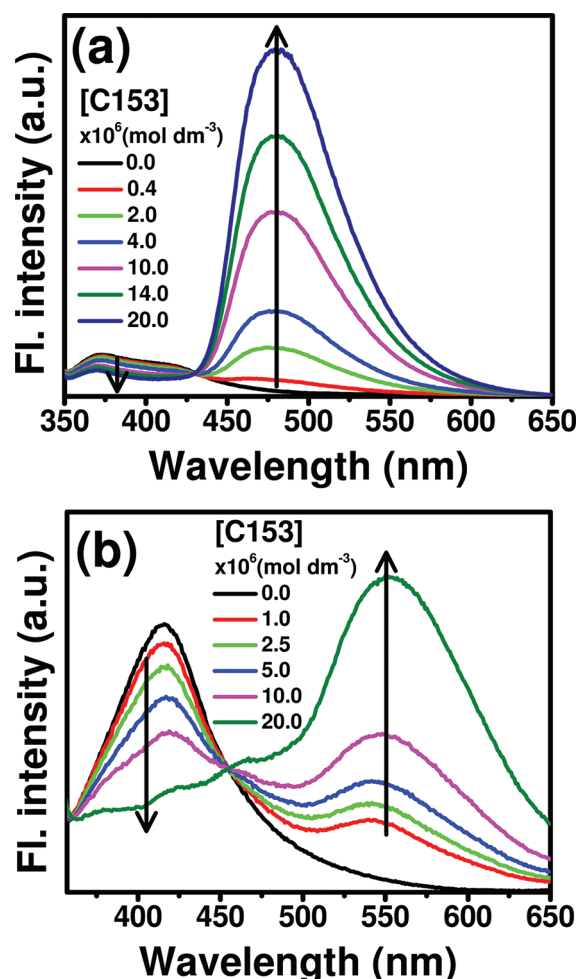


Figure 2. Fluorescence spectral variation of PNVC ($\sim 2 \times 10^{-5}$ mol dm^{-3}) in (a) toluene and (b) water with the addition of C153. Dye concentrations are provided in the legends. $\lambda_{\text{exc}} = 340$ nm.

analysis. The fluorescence lifetimes of carbazole in toluene and water media are determined independently to be 7 ± 0.2 and 10.0 ± 0.2 ns, respectively.⁵⁹ A similar lifetime component is not observed with the PNVC polymer in either of the solvents. That carbazole emission is absent in the PNVC fluorescence has also been confirmed by Davidson et al.⁵⁶ They have given a convincing explanation to substantiate it as well.⁵⁶ Thus, neither the steady state nor the time-resolved measurements give any indication of emission from the monomeric carbazolyl moiety.¹⁸ Time-resolved emission spectral (TRES) analysis reveals that the high energy partially overlapped excimer develops within 1–2 ns (depending upon the solvent) of the photoexcitation, while the low energy emitting sandwich excimer takes a longer time for its formation. This suggests that the high energy excimer arises from the dimers where the necessary geometrical requirements for the excimer formation exist prior to the photoabsorption.^{10,56,60} Although the precursor for the formation of the sandwich excimer is yet to be confirmed, the possibilities for its formation are either from the reorganization of the high energy excimer or from the direct interaction of an excited carbazolyl and a ground state carbazolyl chromophore.⁶² As stated above, we did not find any signature of the existence of the excited carbazolyl unit (since that would lead to a fluorescence characteristic to carbazole). Hence, formation of the sandwich excimer from the

interaction of the excited state carbazolyl unit with its ground state counterpart is ruled out. Thus, we assign the formation of the low energy excimer from the reorganization of the high energy partially overlapped excimer only. Studies on the excimer formation also suggest that the low energy excimer is formed from the high energy excimer in the photoexcited state and an equilibrium exists between them.^{10,18,58,61,62}

The lifetime of the acceptor (C153) is independently monitored at the emission band of the species at 480 nm in toluene and 550 nm in water exciting the system at 403 nm. C153 shows a monoexponential decay profile with a lifetime of 5 ± 0.4 ns in toluene, while in water a biexponential decay profile with an average lifetime of 2 ± 0.2 ns is observed.^{57,63}

It is interesting to note that in both solvents the donor emissions reveal faster decays upon addition of C153, thereby reflecting a gradual shortening of the fluorescence lifetime of the emitting donor species (Figure 3). The decrease in the

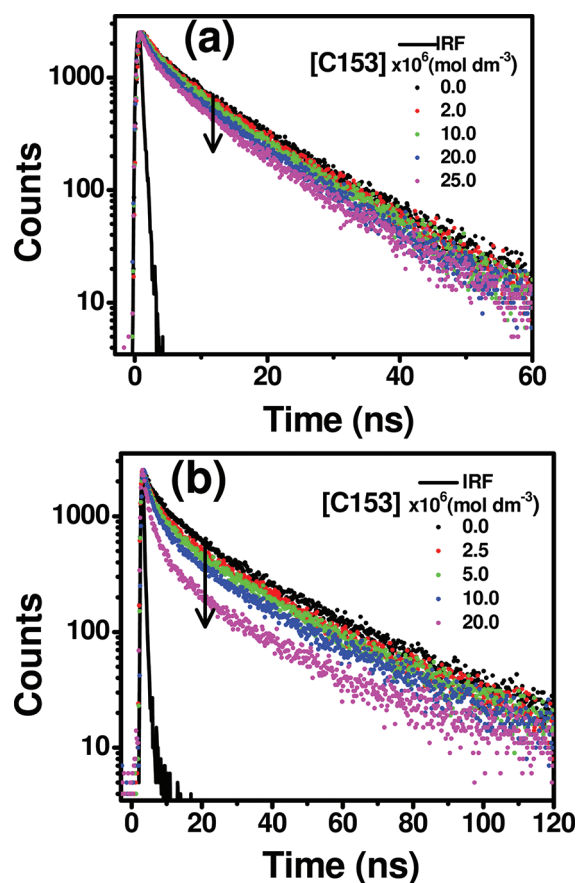


Figure 3. Time-resolved fluorescence decays of PNVC in (a) toluene and (b) water in varying concentrations of C153 ($\lambda_{\text{exc}} = 295$ nm, $\lambda_{\text{em}} = 400$ nm in toluene and 435 nm in water). The concentrations of C153 are provided in the legends. The sharp profile in black is the instrument response function.

donor lifetime on the advent of the acceptor is the revelation of the fact that transfer of fluorescence energy from the excimers of PNVC to C153 occurs exclusively in the photoexcited state.

Figure 3 reveals that in both the solvents addition of C153 leads to a differential quenching of the short-lived and long-lived excimers of PNVC, quenching of the short-lived species being visibly greater than the longer-lived one. Since the fluorescence of PNVC is known to originate from the two distinct excimer species, this interesting observation of the

differential quenching of the lifetimes of the two emitting components in the presence of C153 encouraged us to resolve the involvement of the two excimers toward the energy transfer process.

Figure 4 represents the fluorescence decay profiles of PNVC in toluene at various wavelengths in the range 370–440 nm. All

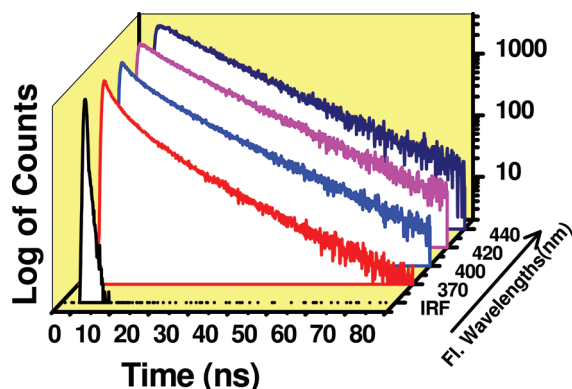


Figure 4. Time-resolved fluorescence decays of PNVC ($\lambda_{\text{exc}} = 295$ nm) in toluene at various emission wavelengths as indicated in the tick labels. The sharp profile in black is the instrument response function.

the decays are found to be biexponential in nature. However, on moving the monitoring wavelength from 370 to 440 nm, the relative contribution of the shorter-lived component goes on decreasing while that of the longer one is increased (Table 1).⁶⁴

Table 1. Fluorescence Decay Times of PNVC ($\lambda_{\text{exc}} = 295$ nm) in Toluene Varying the Emission Wavelengths within 370–440 nm ($\chi^2 = 1.0\text{--}1.2$)

λ_{em} (nm)	τ_1 (ns) (± 0.2)	a_1	τ_2 (ns) (± 0.4)	a_2
370	2.5	0.83	11.9	0.17
400	2.5	0.46	12.0	0.54
420	2.46	0.15	12.4	0.85
440	2.2	0.08	12.3	0.92

This analytical approach demonstrates that the shorter lifetime component of PNVC fluorescence corresponds to the high energy excimer while the longer one to the low energy excimer. The time-resolved area normalized emission spectral (TRANES) study resolves the emission spectra of the individual excimers.¹⁸ Existence of an equilibrium in the photoexcited state between the two excimers as proposed by Hoyle et al. from time-resolved emission spectral (TRES) study⁶² has also been unambiguously established by us from the TRANES study.¹⁸

Quenching of the short-lived component of PNVC to a greater extent compared to the longer-lived one in the presence of a definite concentration of C153, thus, implies a differential involvement of the two excimers in the Förster resonance energy transfer (FRET) process. The data reveals a dominant contribution of the high energy partially overlapped excimer over the low energy fully overlapped one toward the process. With FRET being a long distance dipole induced process, the differential FRET efficiency can be rationalized from a consideration of the dipole moments of the two excimers (donors) and C153 (acceptor). For the energy minimized structures, the calculated ground state dipole moments of the partially overlapped and the sandwich dimeric structures come

out to be 1.68 and 2.55 D, respectively. Since there is no solvent shift in the absorption/excitation maxima of PNVC as we move from toluene to water,¹⁸ the solvent shifts of the fluorescence band maxima, as stated above, have been exploited to estimate the difference between the excited and ground state dipole moments using the modified Lippert equation.³⁵ The excited state dipole moments of the two excimers of PNVC are then determined from these differences and the ground state dipole moments. For the partially overlapped and the sandwich excimers, the excited state dipole moments are thus estimated to be 7.04 and 4.08 D, respectively. Considering the fact that C153 has a nonzero (calculated to be 5.83 D) dipole moment, an appreciably higher dipole moment of the partially overlapped excimer compared to that of the sandwich excimer justifies a better dipole–dipole interaction with the acceptor and hence a greater FRET efficiency of the former compared to its counterpart. It is pertinent to mention here that the relative orientation of the dipoles of the donor and the acceptor should also be a factor to control the FRET efficiency. However, considering the acceptor C153 to be a small molecule, we assume that it randomizes by fast rotational diffusion prior to the energy transfer (*vide* section 3.3) to take place. Thus, the partially overlapped excimer with a higher dipole moment dominates in the energy transfer process over the sandwich excimer with a lower dipole moment.

That the energy transfer process is occurring in the excited state and it is none other than the FRET process is corroborated from the observation of a growth in the time-resolved fluorescence of the acceptor. While exciting the donor (PNVC) system in toluene solvent in the presence of a small amount of the acceptor (C153), the time-resolved fluorescence of C153 monitored at 480 nm (maximum of the acceptor emission) reveals a growth. Figure 5 shows the growth profiles of the acceptor fluorescence in the presence of a definite concentration of the donor and different concentrations of the acceptor in toluene. A gradual shortening of the growth time with an increase in the acceptor concentration is consistent

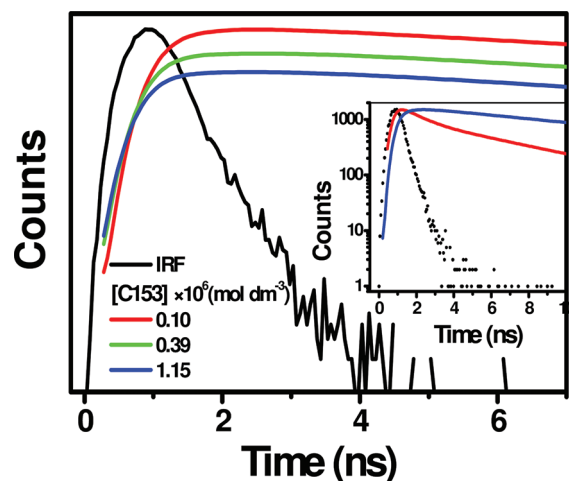


Figure 5. Growth of the fluorescence of C153 in the presence of 2.0×10^{-5} mol dm^{-3} PNVC at varying concentrations of C153 in toluene. Concentrations of C153 are provided in the legends. The sharp profile in black is the instrument response function (IRF). $\lambda_{\text{exc}} = 295$ nm, $\lambda_{\text{em}} = 480$ nm. Inset: Fitted time-resolved fluorescence decays of PNVC (red line) and C153 (blue line) in toluene. The sharp profile in black is the IRF. $\lambda_{\text{exc}} = 295$ nm, λ_{em} is 400 nm for PNVC and 480 nm for C153. The concentration of C153 is 1.0×10^{-7} mol dm^{-3} .

with the expectation for an excited state process, the rate of which increases with an increase in the reactant concentration. The inset of Figure 5 depicts the time-resolved fluorescence decay patterns of a set of fluorescences of the donor and the acceptor under the same experimental conditions. As already stated on increasing the concentration of C153 in the polymer solution, the growth time of the acceptor fluorescence decreases associated with the shortening of the decay time of the short-lived excimer emission. Importantly, for a range of concentrations of the added acceptor, there remains a correspondence between the decay times of the short-lived component of PNVC emission with the growth times of the fluorescence of C153 (Table 2). A good correspondence

Table 2. Fluorescence Decay Times of PNVC and the Growth Times of C153 in the Presence of Varying Concentrations of C153 in Toluene^a

[C153] × 10 ⁶ (mol dm ⁻³)	0	0.096	0.39	1.15	3.8	12.9
Decay of PNVC at 400 nm (ns)	2.5	1.75	1.6	1.47	1.30	1.2
Growth of C153 at 480 nm (ns)		1.75	1.53	1.42	1.30	1.13

^aλ_{exc} = 295 nm, λ_{em} = 400 nm (PNVC) and 480 nm (C153).

between the decay times of the donor emission and the growth times of the acceptor emission unambiguously confirms the formation of the excited species of the acceptor from the donor *via* Förster resonance energy transfer. A similar correspondence is, however, not evident in aqueous solution. This is ascribed jointly to the short fluorescence lifetime of C153 in water (~1.7 ns)⁵⁷ and the slow instrument response (~1 ns) of our setup.

3.3. Calculation of FRET Parameters. After confirming that the energy transfer process is FRET, we intend to decipher the role of the two excimers of the donor PNVC system toward the quenching process. At the same time, for a FRET process, it is important to read the process through calculation of the FRET related parameters like Förster's distance (R_0) at which the efficiency of energy transfer is 50%, the mean distance (r) between the donor and the acceptor, and the energy transfer efficiency (E). To address the aspects, we take the help of both the steady state and time-resolved fluorometric data.

Figure 6 depicts the Stern–Volmer plots from the steady state as well as the lifetime of the high energy excimer. The slopes of the plots give the K_{SV} values. The near correspondence between the Stern–Volmer plots from the steady state fluorescence quenching data and that from the quenching data of the short lifetime component of the donor on the advent of the acceptor confirms that the high energy partially overlapped excimer of PNVC contributes mostly to the FRET process. The agreement between the K_{SV} values obtained from the steady state and the time-resolved data further rules out the involvement of any radiative or trivial energy transfer through re-absorption (*vide infra*). K_{SV} determined in toluene from the steady state quenching and from the quenching of the high energy excimer come out to be $3.3 (\pm 0.1) \times 10^4$ and $3.0 (\pm 0.1) \times 10^4 \text{ mol}^{-1} \text{ dm}^3$, respectively, while the same in water are estimated to be $6.77 (\pm 0.2) \times 10^4$ and $6.23 (\pm 0.2) \times 10^4 \text{ mol}^{-1} \text{ dm}^3$, respectively. k_Q s from the quenching of the short lifetime components (using $\tau_0 = 2.5$ ns in toluene and 6.86 ns in water) come out to be $1.2 (\pm 0.1) \times 10^{13}$ and $9.08 (\pm 0.2) \times 10^{12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively, in toluene and water. The extracted K_{SV} and k_Q values are too high

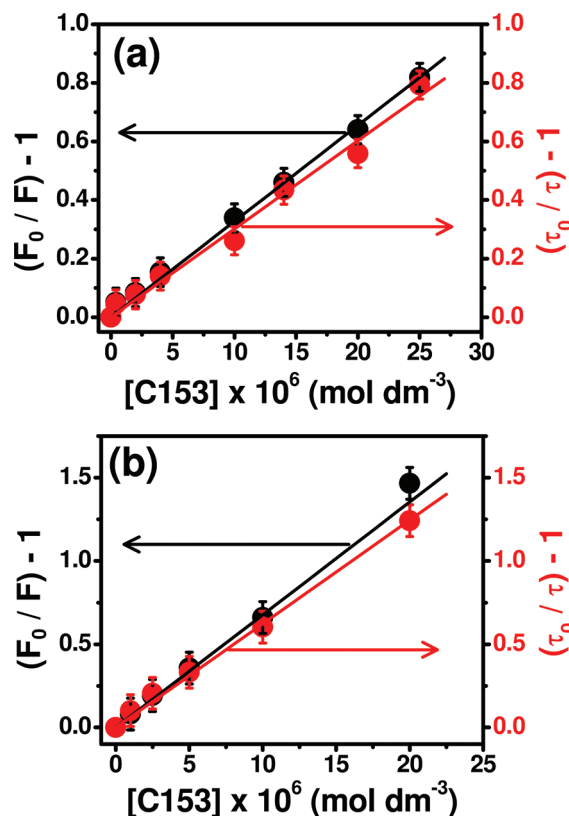
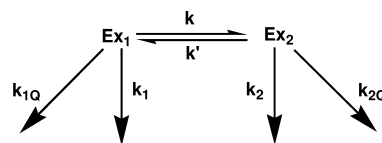


Figure 6. Stern–Volmer plots for the quenching of the fluorescence of PNVC upon addition of C153 from both steady state (black) and fluorescence lifetime of the high energy excimer (red) in (a) toluene and (b) water.

(see later) to assign the fluorescence quenching process to be diffusion controlled collisional quenching. Rather, they are well within the range of FRET as reported in the literature with other systems.³⁵ Thus, the whole set of experiments imply that the mechanism for the fluorescence quenching of PNVC is exclusively FRET in both solvents. Although our experiments reveal the occurrence of FRET from PNVC to C153 in both toluene and water, for the present program, we do not intend to study the role of the solvent on the FRET process. The following scheme (Scheme 2) provides an overview of the

Scheme 2. Scheme Representing the Photophysics of the Excimers of PNVC



photophysics of PNVC in the presence of C153 and hence the differential participation of the excimers in the energy transfer process.

Ex₁ and Ex₂ represent the high energy emitting partially overlapped and the low energy emitting fully overlapped excimers in their photoexcited states, respectively; k_1 and k_2 are the corresponding intrinsic decay constants. k and k' are the rate constants for the forward and backward reactions prevailing in the equilibrium between the two excimers in the excited state; k_{1Q} and k_{2Q} are the respective quenching

constants of the high and low energy excimers for the energy transfer process upon addition of the quencher. Following Scheme 2, we have determined the values of individual quenching constants. The values of k_{1Q} and k_{2Q} come out to be 1.04×10^{13} and $1.23 \times 10^{12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ for the partially and the fully overlapped excimer, respectively, in toluene medium. The said constants in aqueous medium are determined to be 8.67×10^{12} and $8.13 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively. An order of magnitude higher k_{1Q} compared to k_{2Q} establishes the differential participation of the two excimers in the energy transfer process.

The efficiency (E) of FRET depends not only on the distance between the donor and the acceptor (r) but also on the critical energy transfer distance (R_0) expressed by the following relation

$$E = R_0^6 / (R_0^6 + r^6) \quad (2)$$

where R_0 is the characteristic distance, called the Förster's distance or critical distance, at which the efficiency of energy transfer is 50%. The magnitude of R_0 depends on the spectral properties of the donor and the acceptor molecules.⁶⁵ Since the above discussion establishes the quenching process to be exclusively FRET, the overall energy transfer efficiency (E) is calculated from the fluorescence lifetime of the short-lived excimer of the polymer using the following relation

$$E = 1 - \tau / \tau_0 \quad (3)$$

where τ and τ_0 are the fluorescence lifetimes of the donor in the presence and in the absence of the acceptor, respectively. Energy transfer efficiencies (E) are determined at various concentrations of the acceptor in both the media.

The dependence of R_0 on the spectral overlap (Figure 7) of the donor and the acceptor systems is expressed through the following equation

$$R_0^6 = 8.8 \times 10^{23} [\kappa^2 \cdot n^{-4} \cdot \Phi_D \cdot J(\lambda)] \text{ (Å}^6\text{)} \quad (4)$$

where κ^2 is the factor expressing the relative orientation of the donor to the acceptor molecule, n is the refractive index of the medium (1.4969 for toluene and 1.333 for water),⁶⁶ Φ_D is the quantum yield of the donor in the absence of the acceptor, and $J(\lambda)$ is the overlap integral of the fluorescence emission spectrum of the donor and the absorption spectrum of the acceptor in units of $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^3$. κ^2 is assumed to be 2/3 considering that the donor and acceptor randomize by rotational diffusion prior to the energy transfer.³⁵ The quantum yields of PNVC in toluene ($\Phi_f = 0.007$) and water ($\Phi_f = 0.011$) have been determined relative to the quantum yield of quinine sulfate in water ($\Phi_f = 0.546$). $J(\lambda)$ has been calculated from the numerical integration method using the following relation.^{35,37}

$$J(\lambda) = \frac{\int_0^\infty F(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda}{\int_0^\infty F(\lambda) d\lambda} \quad (5)$$

where $F(\lambda)$ is the corrected fluorescence intensity of the donor in the wavelength range λ to $(\lambda + \Delta\lambda)$ with the total intensity normalized to unity and $\epsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor at wavelength λ expressed in $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. The overlap integrals $J(\lambda)$ for the PNVC–C153 pair in toluene and water media are estimated to be 3.37×10^{-14} and $7.53 \times 10^{-14} \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^3$, respectively.

The energy transfer efficiencies calculated using the quenching of the shorter lifetime component corresponding

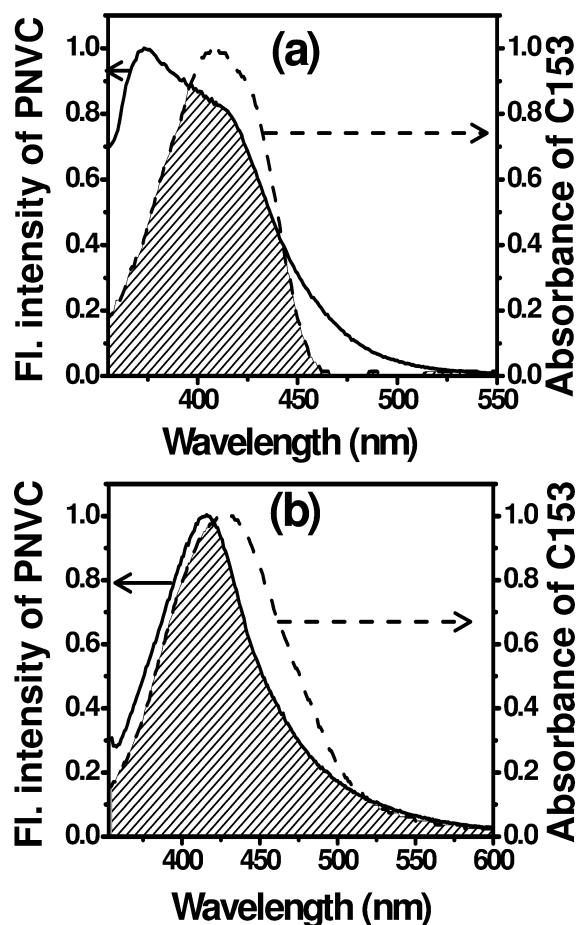


Figure 7. Overlaps between the emission spectrum of PNVC (donor) and the absorption spectrum of C153 (acceptor) in (a) toluene and (b) water.

to the high energy partially overlapped excimer come out to be 0.36 and 0.55 in toluene and water, respectively, at 1:1 conditions of donor–acceptor pair using eq 3. Figure 8 depicts the FRET efficiencies in the presence of varying concentrations of C153 in toluene and water. The critical energy transfer

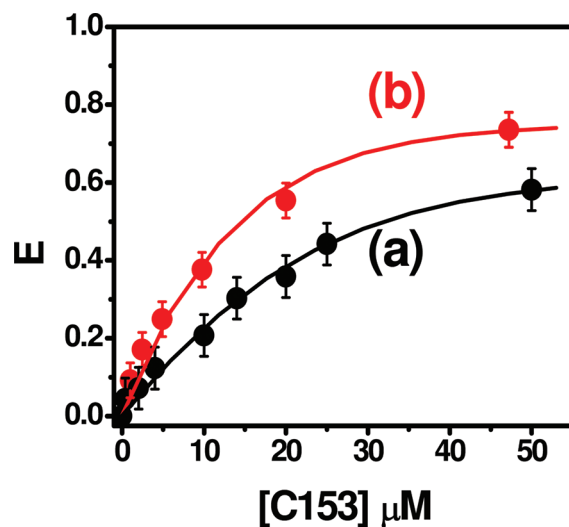


Figure 8. Variation of the energy transfer efficiency (E) as a function of concentration of C153 in (a) toluene and (b) water.

distances (R_0) in toluene and water have been estimated to be 17.4 and 23.2 Å, respectively.

4. CONCLUSIONS

The study demonstrates an efficient Förster resonance energy transfer (FRET) from the two excimers of the nonconjugated polymer PNVC to the laser dye C153. The results imply that the two excimers of PNVC exhibit differential participation toward the energy transfer process: the high energy partially overlapped shorter-lived excimer contributing dominantly. A difference in the dipole moments of the two excimers provides the template for their differential behavior toward the FRET process. This differential behavior of the two excimers of PNVC has a potential to be exploited for developing selective electronic switches. The energy transfer from PNVC to C153 results in the red emission of the dye which could be exploited in designing the color tuning of PLEDs. The energy transfer from the host polymers to the dye dopants has practical applications in sensing, ranging from the detection of the chemical and biological analytes to explosives.

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Notes

The authors declare no competing financial interest.

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