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Involvements of phenyldibenzophosphole and 9-phenylcarbazole in electron transfer reactions with photoexcited 9-cyanoanthracene

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Abstract

9-Cyanoanthracene (9CNA), used as an electron acceptor, has been subjected to photoexcitation in the presence of both the electron donors, phenyldibenzophosphole (PDP) and 9-phenylcarbazole (9PC). Steady state and time resolved (fluorescence lifetime by time correlated single photon counting and laser flash photolysis) spectroscopic measurements were made both in non-polar *n*-heptane (NH) and polar aprotic acetonitrile (ACN) at the ambient temperature. The spectroscopic studies coupled with electrochemical measurements by cyclic voltammetry demonstrate the presence of photoinduced electron transfer (PET) processes with the present donor–acceptor systems in polar ACN. In non-polar NH, the nature of the mechanism involved in quenching of fluorescence of the acceptor 9CNA differs significantly. The donor 9PC, in such a non-polar environment, undergoes partial charge separation reactions with the excited singlet 9CNA and forms radiative exciplex, whereas formation of such exciplex was not apparent in case of the other donor PDP. It is presumed, both from steady state and time resolved fluorescence studies, that the exciplex, if forms from the interaction between PDP and the excited 9CNA may undergo very fast non-radiative decay possibly through intersystem crossing or some other channels. From the electrochemical measurements, steady-state fluorescence, transient absorption spectra and analysis of transient decays, measured in ACN, formation of radical ion-pair species both in the excited singlet and triplet states has been inferred. In ACN, triplet population of 9CNA from charge (ion-pair) recombination mechanism was apparent from transient absorption decay and supported by thermodynamical calculations but this phenomenon was not observed in NH due to lack of formation of triplet ion-pair in such medium. The observed results indicate that in non-polar medium NH, the radiative nature of the exciplex formed in the excited singlet state of 9CNA in the presence of 9PC changes to the non-radiative one when the other donor PDP containing the heavy atom “phosphorous” is used as a reacting species in place of 9PC.

Keywords: Photoinduced electron transfer; Dynamic and static modes; Exciplex; Ion-pair recombination mechanism; Non-radiative process

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1. Introduction

The photophysics and photochemistry of heteroaromatic molecules like carbazole derivatives have already been proved to be very rich field of study [1–15]. *N*-alkyl and *N*-aryl derivatives, in addition to carbazole itself, along with poly(*N*-vinylcarbazole) [1,16–20] and other polymers and copolymer systems containing the carbazole group [21–23] have been investigated in different environments. Highly exergonic photoinduced electron transfer (PET) reactions within several bichromophores of substituted carbazoles and nitrofluorene systems linked by polymethylene spacers have been investigated by steady state and picosecond laser flash photolysis techniques [11]. The corresponding oligomer systems of the above bichromophores where the bichromophores are present as pendant groups were also studied both by time resolved and xerographic techniques to examine their photoconducting properties [11]. In fact the above bichromophores and the corresponding oligomers show very efficient photoconducting properties having significant commercial importance [24,25]. In the field of electron transfer, considerable interest has been shown in carbazole systems but very little attention has been given to studying its phosphorus analog, dibenzophosphole. However, it is very difficult to perform spectroscopic studies with dibenzophosphole due to its air sensitivity. For this reason some photophysical investigations

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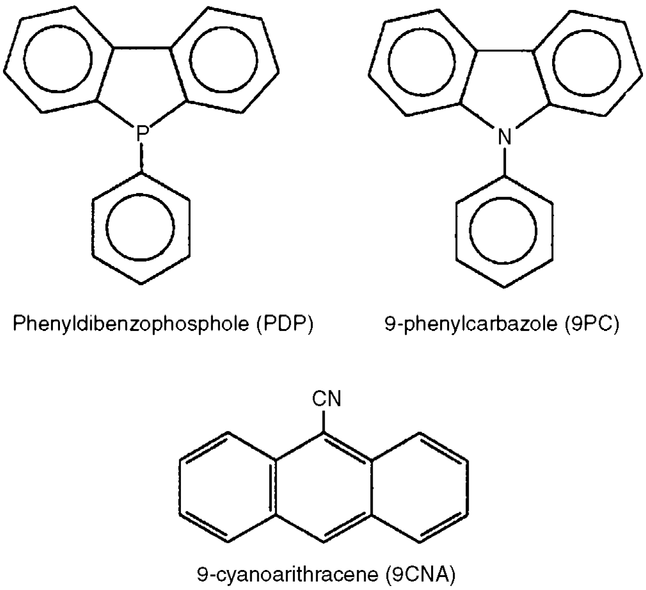

Fig. 1. Molecular structures of PDP, 9PC and 9CNA.

were done before in solutions and polymeric environments employing phenyldibenzophosphole (PDP) [9,10] whose air sensitivity is such that it can be stored without recourse to an inert atmosphere though an inert atmosphere was used for its initial preparation and purification [9,26]. Many investigations on photoinduced electron transfer (PET) reactions were performed using carbazole, *N*-alkyl and *N*-aryl carbazole derivatives [4,12] but very little attention has been paid to PDP which is supposed to serve as an electron donor in the presence of suitable electron acceptor molecules. It may be anticipated that in the case of PDP, the heteroaromatic containing the heavy atom phosphorus should, relative to other carbazole and *N*-aryl carbazoles, efficiently produce triplet states due to internal heavy atom effect. In the present work the PET reactions have been investigated using PDP and the structurally similar compound 9-phenylcarbazole (9PC) (Fig. 1) to compare the nature of mechanisms of their electron transfer (ET) reactions with the well-known electron acceptor 9-cyanoanthracene (9CNA) both in non-polar and highly polar media. Special attention has been given to examining the role of surrounding solvents and the heteroatom of the carbazolyl moiety on the efficiency of electron transfer processes. In addition to electrochemical measurements using cyclic voltammetry, studies were mainly made by steady state and time resolved spectroscopic, laser flash photolysis and time correlated single photon counting, techniques.

2. Experimental

2.1. Materials

PDP was synthesized by the method described elsewhere [9] and was finally purified by multiple recrystallizations from ethanol in a nitrogen atmosphere. Some experiments were also carried out on PDP samples purified in this method but with the additional step of vacuum sublimation. The vacuum-sublimed material gave the same results as the recrystallized material. The other two samples 9PC (99% pure) and 9CNA (97% pure), supplied by Aldrich, were purified by the methods of recrystallization and vacuum sublimation, respectively. The solvents *n*-heptane (NH) (SRL), ethanol (EtOH) (E. Merck) and acetonitrile (ACN) (SRL) of spectroscopic grade were distilled under vacuum according to the standard procedure and tested before use for any impurity emission in the wavelength region concerned.

2.2. Spectroscopic apparatus

Steady-state electronic absorption and fluorescence emission spectra of dilute solutions (10^{-2} to 10^{-6} mol dm^{-3}) of the samples were recorded, at ambient temperature (296 K), using 1 cm path length rectangular quartz cells by means of an absorption spectrophotometer (Shimadzu UV–vis 2101 PC) and F-4500 fluorescence spectrophotometer (Hitachi), respectively. Fluorescence lifetimes were measured by using a time-correlated single photon counting (TCSPC) fluorimeter constructed from components purchased from Edinburgh Analytical Instruments (EAI), model 199, UK. The experimental details are given elsewhere [4]. The goodness of fit has been assessed with the help of statistical parameters χ^2 and DW. All the solutions prepared for the lifetime measurements were deoxygenated by purging with an argon gas stream for about 30 min. Another arrangement was made for lifetime measurements, where the samples were excited at 405 nm using a picosecond diode laser (IBH Nanoled-07). The emission was collected at a magic angle polarization using a Hamamatsu MCP photomultiplier (2809U). The time correlated single photon counting (TCSPC) setup consists of an Ortec 935 QUAD CFD and a Tennelec TC 863 TAC. The data is collected with a PCA3 card (Oxford) as a multichannel analyzer. The typical FWHM of the system response is about 80 ps.

A special dewar in which a long cylindrical quartz tubing (cell) of 3 mm in diameter could be introduced, was used for low temperature (77 K) measurements.

2.3. Laser flash photolysis

Triplet absorption spectra were measured using nanosecond flash photolysis set up (Applied Photophysics) containing an Nd:YAG laser (DCR-11, Spectra Physics). The sample was excited by 355 nm laser light (FWHM = 8 ns). Triplet spectra were monitored through absorption of light from a pulsed Xe lamp (250 W). The photomultiplier (IP28) output was fed into a combiscope (Fluke PM3394B, 200 MHz) and the data were analyzed using Fluke View Combiscope software.

2.4. Electrochemical measurements

The redox potentials of the reactants, in ACN solvent, were determined by cyclic voltammetric method using the PAR model 370-4 electrochemistry system. Three electrode systems including SCE as a standard were used in the measurements. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte [4].

3. Results and discussion

3.1. Electrochemical measurements

From electrochemical measurements using cyclic voltammetry the redox potentials of PDP, 9PC and 9CNA were determined in ACN solvent. The half-wave oxidation potentials of PDP and 9PC were found to be +1.39 and +1.28 V, respectively (Table 1). It appears that the introduction of the phosphorus atom reduces the electron donating capability of the carbazolyl moiety. The driving energy values, ΔG^0 in eV, in ACN were computed using Eq. (1) [27–30] as the difference of the redox (polarographic) potentials of the electron donor and the acceptor in ACN and the lowest singlet excited state energy ($E^*_{0,0}$) of the acceptor.

$$\Delta G^0 = E^{\mathrm{OX}}_{1/2}(D/D^+) - E^{\mathrm{RED}}_{1/2}(A^-/A) - E^*_{0,0} \qquad (1)$$

The Coulomb stabilization term has been neglected in highly polar solvent ACN because its contribution was found to be very small (∼ 0.06 eV) [11]. ΔG^0 values estimated from the Eq. (1) (Rehm–Weller relation) were found to be −0.56 and −0.67 eV for the systems PDP + 9CNA* and 9PC + 9CNA*, respectively (Table 1). 9CNA* denotes the excited singlet electronic state of 9CNA. The negative values of ΔG^0 indicate that thermodynamically there is possibility of occurrence of PET reactions between the ground state donor PDP and 9PC and the excited electron acceptor 9CNA in ACN medium.

Since redox potentials in non-polar NH could not be measured, an attempt was made to estimate the approximate shift in the value of ΔG^0 on going from ACN to NH medium using the expression (2) [31,32] below:

$$\Delta G^0(\mathrm{solvation}) = -\left(\frac{e^2}{8\pi\epsilon_0}\right)\left(\frac{1}{r_\mathrm{D}} + \frac{1}{r_\mathrm{A}}\right)\left(1 - \frac{1}{\epsilon_\mathrm{s}}\right) \qquad (2)$$

The shift was computed and the value was +1.47 eV. Following Weller assumption [33] the Coulombic term was fixed at 0.2 eV for all D–A pairs in non-polar medium NH. So, for the present D–A systems,

$$\Delta G^0(\mathrm{NH}) = \Delta G^0(\mathrm{ACN}) + 1.27 \qquad (3)$$

Using the above relation, ΔG^0 values for PDP + 9CNA* and 9PC + 9CNA* systems were estimated to be +0.71 and +0.60 eV, respectively (Table 1). These results indicate the slim possibility of occurrence of photoinduced ET reactions within the excited 9CNA and ground PDP (or 9PC) molecules in such non-polar environment.

3.2. Steady-state spectroscopic measurements

Both in NH and ACN fluid solutions at the ambient temperature, the electronic absorption spectra of the mixture of the donor PDP or 9PC and the acceptor 9CNA appear to be just a superposition of the corresponding spectra of the individual reactants. This indicates the lack of formation of any charge transfer complex within the above reacting species in the ground state. However, in ACN the steady-state fluorescence emission spectrum of the acceptor 9CNA is found to be diminished significantly (Fig. 2a-b) over the entire band envelop in the presence of both the donor molecules. The concentrations of the donor used to measure the fluorescence quenching of 9CNA were found to be ineffective to produce any change in the electronic absorption spectra of 9CNA. Moreover, since at the wavelength 403 nm, used for exciting the fluorescence spectra of 9CNA, the donor molecules are transparent, the role of inner filter effect seem to be negligible in the quenching mechanism of 9CNA fluorescence.

In non-polar NH, the changes that occurred in the fluorescence emission spectra of 9CNA in the presence of the donor 9PC were not uniform throughout the whole spectral range (Fig. 3). However, in the presence of the donor PDP, the quenching of 9CNA fluorescence was observed

Table 1
Values of redox potentials of the reactive sites and Gibbs free energy changes (ΔG^0) associated with photoinduced ET processes for the present D–A systems at 296 K

System[a]	$E^{\mathrm{OX}}_{1/2}(D/D^+)$ (V) (±5 mV)	$E^{\mathrm{RED}}_{1/2}(A^-/A)$ (V) (±5 mV)	$E^*_{0,0}$	$\Delta G^{0\mathrm{b}}$(eV)
PDP + 9CNA + ACN	+1.39	−1.13	–	+2.52
PDP + 9CNA* + ACN	+1.39	−1.13	3.08	−0.56
9PC + 9CNA + ACN	+1.28	−1.13	–	+2.41
9PC + 9CNA* + ACN	+1.28	−1.13	3.08	−0.67
PDP + 9CNA + NH	+1.39	−1.13	–	+3.79
PDP + 9CNA* + NH	+1.39	−1.13	3.08	+0.71
9PC + 9CNA + NH	+1.28	−1.13	–	+3.68
9PC + 9CNA* + NH	+1.28	−1.13	3.08	+0.60

[a] denotes the lowest excited singlet state (S_1).

[b] $E^*_{0,0}$ is the singlet–singlet (0,0) transition energy of the excited chromophore.

throughout the whole spectral range. This is similar to the observation made in polar ACN solvent. The nature of the quenching mechanisms was found to be different in polar ACN and non-polar NH media. The details are given below.

3.3. *Time correlated single photon counting measurements*

Irrespective of the polarity of the surrounding solvent, the fluorescence lifetime (τ_0) of 9CNA is found to be significantly quenched in the presence of the quencher (donor PDP or 9PC). Nevertheless, in highly polar solvent ACN and at a particular concentration of the donor (f_0/f) was found to be nearly equal to, within the experimental error, (τ_0/τ) ("f" stands for steady-state fluorescence emission intensity of 9CNA at a particular concentration of the donor (quencher), the subscript "0" corresponds to the 9CNA fluorescence intensity (or lifetime) without quencher, "τ" denotes the quenched lifetime of 9CNA in the presence of the donor). The above observations demonstrate the dynamic nature of the quenching phenomena occurring with the donor (quenchers PDP and 9PC) and acceptor (fluorescer) 9CNA molecules in ACN solvent. But in non-polar NH environment, though fluorescence lifetime quenching was observed but $(f_0/f) \neq (\tau_0/\tau)$. At a particular concentration of the quencher, the magnitude of (f_0/f) was found to be higher than that of (τ_0/τ) $((f_0/f) > (\tau_0/\tau))$.

The above observations reveal that in NH mixture of both dynamic and static modes may be involved in quenching mechanisms which have been further examined (vide infra).

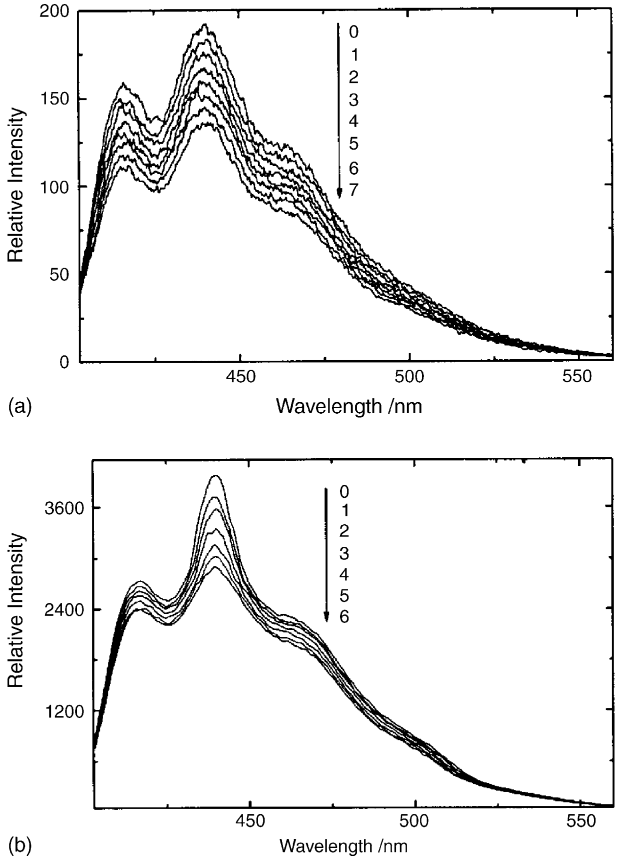

Fig. 2. Steady-state fluorescence emission spectra (λ_{ex} = 403 nm), in ACN fluid solution of (a) 9CNA (conc. ~ 5.05 × 10^{-6} mol dm^{-3}) with different concentrations (mol dm^{-3}) of PDP in (0) 0: (1) 3.26 × 10^{-4}; (2) 6.52 × 10^{-4}; (3) 9.79 × 10^{-4}; (4) 1.30 × 10^{-3}; (5) 1.63 × 10^{-3}; (6) 1.96 × 10^{-3}; (7) 2.28 × 10^{-3}; and (b) 9CNA (conc. ~ 1.54 × 10^{-5} mol dm^{-3}) with different concentrations (mol dm^{-3}) of 9PC in (0) 0: (1) 1.77 × 10^{-4}; (2) 3.54 × 10^{-4}; (3) 5.3 × 10^{-4}; (4) 7.07 × 10^{-4}; (5) 8.84 × 10^{-4}; (6) 1.06 × 10^{-3}, at 296 K.

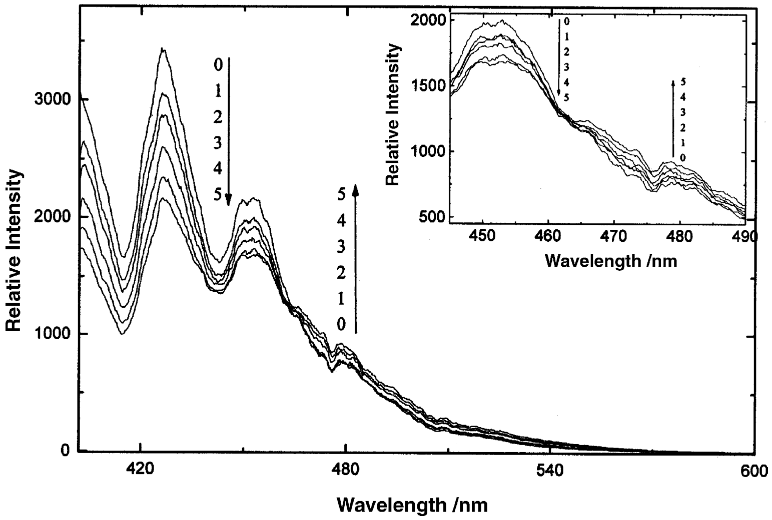

Fig. 3. Steady-state fluorescence emission spectra (λ_{ex} = 403 nm), in NH fluid solution, of 9CNA (conc. ~ 1.25 × 10^{-5} mol dm^{-3}) with different concentrations (mol dm^{-3}) of 9PC in (0) 0: (1) 1.48 × 10^{-3}; (2) 3.12 × 10^{-3}; (3) 7.23 × 10^{-3}; (4) 1.05 × 10^{-2}; (5) 1.43 × 10^{-2} at 296 K. *Inset*: Representation of the same spectra in the wavelength region 445–490 nm.

3.4. Stern–Volmer (SV) plots

The bimolecular fluorescence quenching rate, k_q, was determined in ACN solvent using linear SV plots [34] constructed from the steady state (lowering of fluorescence intensity of 9CNA with quencher concentration) and the time resolved (reduction of fluorescence lifetime of 9CNA with the addition of quencher PDP or 9PC) fluorescence quenching. From both the plots (Fig. 4) nearly similar values of k_q ($\sim 1.4 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) were found for both PDP + 9CNA* and 9PC + 9CNA* systems (Table 2). This observation along with the findings discussed above (Section 3.3) suggests dynamic quenching in highly polar medium ACN. The dynamic mode, in high probability, should be PET as occurrence of non-radiative energy transfer is practically impossible within the reacting partners as the acceptor molecule, whose lowest excited singlet state lies lower than that of the donors, was excited. Thus, it appears that PET has an active role in quenching mechanism. Since ΔG^0 for both the donor–acceptor pairs are around -0.6 eV (Table 1) in ACN, i.e., as the PET reactions fall in the intermediate region ($-0.4\,\mathrm{eV} > \Delta G^0 \gg -2.0\,\mathrm{eV}$), the observed similarities of the k_q values, deduced from SV plots, with the diffusion-controlled limit (k_d for ACN $\sim 1.9 \times 10^{10}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$) are in accord to the views of Kikuchi [35]. It is relevant to mention here that from the emission spectra of both the present donor molecules (Fig. 5), the ϕ_p/ϕ_f (ϕ_p and ϕ_f represent the relative quantum yields of the phosphorescence and fluorescence emissions, respectively) values were estimated to be ~2.7 and 0.7 for PDP and 9PC, respectively, in EtOH rigid glassy matrix at 77 K. These observations demonstrate that due to the presence of the heavy atom “phosphorus”, PDP can efficiently produce triplet through intersystem crossing (ISC) process. However, from the observed similar quenching rate, k_q, values of 9CNA* + PDP and 9CNA* + 9PC systems, it shows that in polar medium ACN heavy atom effect does not play significant role in the mechanism of quenching which seems to be mainly governed by photoinduced ET process.

In the non-polar solvent NH, the quenching of the fluorescence spectra of 9CNA in the presence of PDP exhibits upward curvature in SV plot (Fig. 6). This deviation from linearity may be due to the prevailing of static mode in the quenching reaction mechanisms as observed by earlier authors [36].

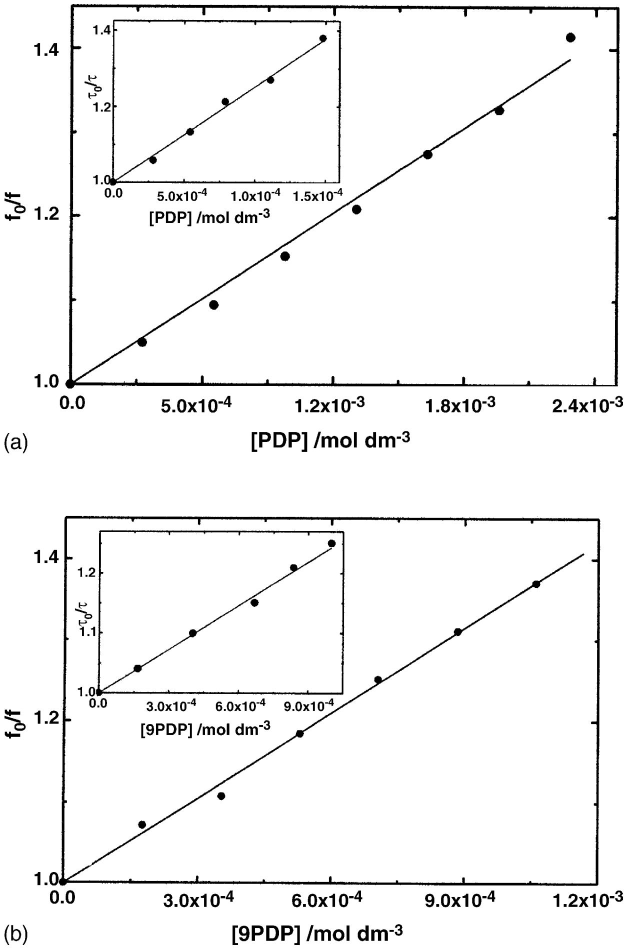

Fig. 4. (a) Stern–Volmer (SV) plots from steady-state fluorescence emission intensity measurements in case of singlet (S_1) excitation of 9CNA in the presence of PDP in ACN fluid solution at 296 K. *Inset*: Stern–Volmer (SV) plots from fluorescence lifetime measurements (time-resolved) in case of singlet (S_1) excitation of 9CNA in the presence of PDP in ACN fluid solution at 296 K. (b) Stern–Volmer (SV) plots from steady-state fluorescence emission intensity measurements in case of singlet (S_1) excitation of 9CNA in the presence of 9PC in ACN fluid solution at 296 K. *Inset*: Stern–Volmer (SV) plots from fluorescence lifetime measurements (time-resolved) in case of singlet (S_1) excitation of 9CNA in the presence of 9PC in ACN fluid solution at 296 K.

Table 2
Fluorescence quenching data for the present D–A systems at 296 K, in ACN solvent

System	τ_0 (ns) (±0.4)	K_{SV} ($\mathrm{dm^3\,mol^{-1}}$)	k_q ($\mathrm{dm^3\,mol^{-1}s^{-1}} \times 10^{10}$)
PDP + 9CNA*+ ACN	17.2	175.2[a]	1.02[b]
		251.9[b]	1.46[b]
9PC + 9CNA*+ ACN	17.2	300.1[a]	1.74[a]
		243.3[b]	1.41[b]

(*) denotes the electronic excited singlet state S_1. τ_0 represents the fluorescence lifetime of 9CNA in the absence of the quencher. K_{SV} is the Stern–Volmer constant. k_q is the dynamic fluorescence quenching rate constant.

[a] These values are obtained from steady-state fluorescence emission intensity measurements.

[b] These values are obtained from time resolved measurements.

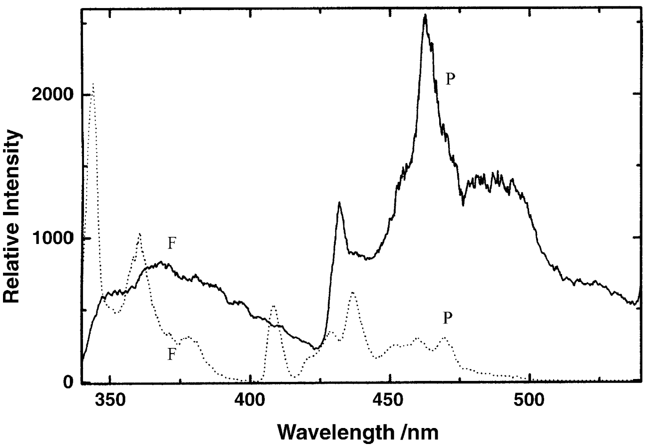

Fig. 5. Fluorescence and phosphorescence spectra of PDP (the solid curve, conc. ~ 3.26×10^{-5} mol dm^{-3}) and 9PC (the dotted curve, conc. ~ 3.14×10^{-5}mol dm^{-3}), in EtOH rigid glassy matrix, at 77 K.

Nevertheless, the gradual reduction of the fluorescence lifetime of 9CNA with the addition of the quencher (donor) PDP indicates that both static and dynamic quenching mechanisms may be involved. The Stern–Volmer plot obtained using quenched fluorescence lifetimes of 9CNA in NH in the presence of PDP is shown in the inset of Fig. 6. A positive deviation (upward curvature) from linearity was observed. This positive deviation in the (τ_0/τ) versus $[Q]$ plot indicates that the quenching of excited singlet of 9CNA by the donor PDP is an irreversible process unlike the situation observed by Rath et al. [37] for naphthacenequinone–aromatic hydrocarbon systems. It seems the 9CNA* molecules interacting with PDP form exciplex (partial charge separated complex) as the intermediate which undergoes very fast non-radiative deactivation before charge recombination (back transfer) occurs. If the back transfer process had been operative to produce the reactants 9CNA* and PDP, (τ_0/τ) versus $[Q]$ plot should undergo a negative deviation from the linearity as observed by earlier authors [37]. From the above observations, the following reaction mechanisms have been proposed:

$$9\text{CNA}^* + \text{PDP} \rightleftharpoons {}^1(9\text{CNA}^{\delta-} \cdots \text{PDP}^{\delta+})^* \xrightarrow[\text{path}]{\text{non-radiative}} 9\text{CNA} + \text{PDP}$$

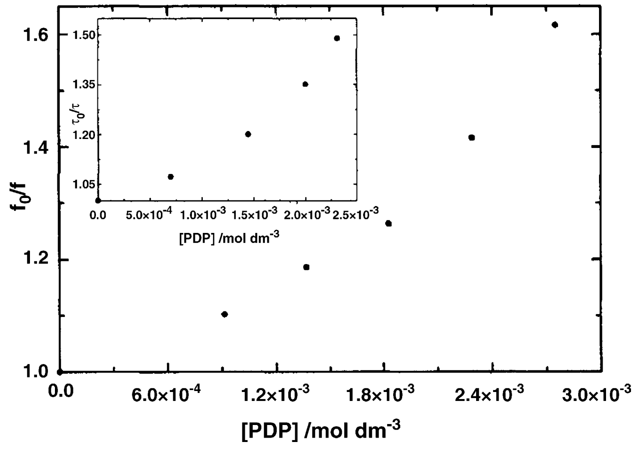

Fig. 6. Stern–Volmer (SV) plots from steady-state fluorescence emission intensity measurements in case of singlet (S_1) excitation of 9CNA in the presence of PDP in NH fluid solution at 296 K. *Inset*: Stern–Volmer (SV) plots from fluorescence lifetime measurements (time-resolved) in case of singlet (S_1) excitation of 9CNA in the presence of PDP in NH fluid solution at 296 K.

In the excited monomer-exciplex equilibrium, the forward path appears to be the dominating channel with increase of concentration of PDP. The non-observable exciplex may be due to the rapid non-radiative deactivation possibly through intersystem crossing channels as PDP contains heavy atom "P". In case of carbazole-heavy atom containing acetic acid systems we reported earlier [38] that the contact exciplex of charge transfer nature formed in the excited singlet state depletes non-radiatively through intersystem crossing (ISC) channel.

In the same non-polar NH environment the situation becomes different when the donor 9PC was used as quencher. Both steady state and time resolved fluorescence studies demonstrate the formation of radiative exciplex unlike the situation observed in the case of the other donor PDP where formation of non-radiative exciplex was apparent.

3.5. Search for exciplex with 9PC quencher

It is observed that with gradual addition of 9PC, the fluorescence quenching of 9CNA in NH occurs non-uniformly throughout the spectra (Fig. 3). On careful inspection it was seen that the reduction of intensity occurs in the domain of 420–450 nm accompanied by the enhancement of the emission at the remaining red part (in the region of 480 nm) of the spectra. An isoemissive point at the position of ~462 nm was observed. It is relevant to point out here that in ACN environment 9PC causes quenching in 9CNA fluorescence intensity around the entire band envelop. It appears that in NH, a radiative exciplex $(\text{D}^{\delta+} \cdots \text{A}^{\delta-})^*$ (partial charge transfer) may be formed between excited 9CNA and ground 9PC.

To locate the exact position of the charge transfer (CT) exciplex band, fluorescence lifetimes were measured monitoring at 430, 450 nm and 480 nm of the spectra. Though from the steady state spectral measurements it seemingly indicates that the exciplex emission resides at around 480 nm but even at 430 nm position the fluorescence emission shows biexponential decay with lifetimes 18.8 ns and 0.40 ns (Table 3). As the unperturbed fluorescence lifetime of 9CNA in NH is ~13 ns, it shows that in presence of 9PC, two types of species are generated. It is logical to presume that the shorter component arises from quenched 9CNA and the longer one corresponds to the decay of the exciplex. As even at 430 nm, the fractional contribution associated with longer lifetime is 0.86 (Table 3), a large portion of the exciplex band is hidden within the band envelop of 9CNA and due to the broad nature of its spectrum, its presence was only detectable through enhancement of the 9CNA emission spectra at around 480 nm (frac-

Table 3
Measured fluorescence lifetimes of 9CNA, in the presence of 9PC, at 296 K, in NH solvent, monitoring at the different wavelengths (λ_{em})

λ_{em} (nm)	τ_0 (ns) [a]	τ_1 (ns) [a]	f_1	τ_2 (ns) [a]	f_2	τ_3 (ns) [a]	f_3	χ^2
430[b]	13.3	18.8	0.86	0.40	0.14	–	–	1.1
450[b]	13.1	18.8	0.89	0.45	0.11	–	–	1.1
480[c]	12.9	18.6	0.96	0.45	0.08	0.41	−0.04	1.2

τ_0 is the fluorescence lifetime of 9CNA in the absence of the quencher. τ_1, τ_2 and τ_3 represent the different components of fluorescence lifetime in the presence of the quencher. f_1, f_2 and f_3 are the corresponding fractional contributions.

[a] The experimental error lies within ±5%.

[b] Double exponential fit was found to be the best fit.

[c] Triple exponential fit was observed to be the best one (see text).

tional contribution of exciplex component becomes 0.96) where monomeric emission of 9CNA was weak.

The observed decrements of fluorescence emission intensity of 9CNA at 430 and 450 nm positions in presence of 9PC seem to be due to the resulting effect of quenching of excited singlet state of 9CNA and appearance of radiative CT exciplex within excited 9CNA and ground state 9PC in NH medium.

As at 480 nm the majority of the emission originates from exciplex, special attention was given to measure the decay at this region for locating the rise, resulted from charge separation, prior to decay. Monitoring the emission at 480 nm, the decay was collected on the short time scale (Fig. 7). Initially a rise was observed followed by a decay. The decay was reliably fitted ($\chi^2 \sim 1.2$) by a triple exponential (Fig. 7) as shown below:

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) \quad (4)$$

The lifetime τ_3 was found to be ~0.4 ns associated with negative preexponential factor (Table 3). The other lifetimes τ_2 (~ 0.45 ns) and τ_1 (~18.6 ns) are very similar to the quenched 9CNA and the exciplex decay times, respectively, i.e., the observed shorter and longer components when monitored at 430 or 450 nm positions. The 0.4 ns (τ_3) should be the rise time (τ_r). As the rise time, τ_r, is similar to the lifetime of the quenched 9CNA (~0.45 ns, Table 3) it may be inferred that the decay of the acceptor fluorescence occurs concurrently with the rise of fluorescence from the exciplex state. This observation demonstrates that the excited acceptor state directly relaxes to the exciplex state.

As the exciplex lifetime is around 18 ns, approximately ($1/e$) of the exciplex intensity should decay out during this time by ion recombination or charge dissociation mechanism. As the measurements were made in non-polar medium, the former channel seems to be relatively much more active.

However, though fluorescence lifetime data reveal that radiative exciplex may be responsible for the observed enhancement of the fluorescence spectra at around 470–480 nm region but no broad band of exciplex was observed in the steady state spectra. Instead the shape of the enhanced spectra looks very similar to that of 9CNA fluorescence. It is possible that the observed spectra may be the superposition of the corre-

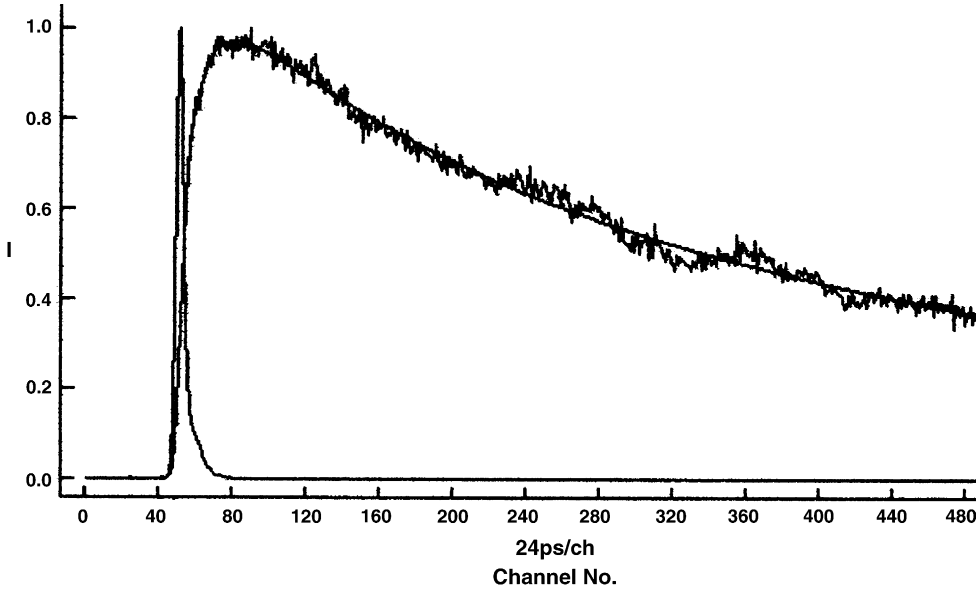

Fig. 7. Fluorescence decay curve associated with laser profile at 480 nm of 9CNA–9PC system, in NH medium, after 403 nm laser irradiation. Triple exponential fitting (see text) shows the best fit (χ^2 ~1.2), the solid line represents the fitted curve.

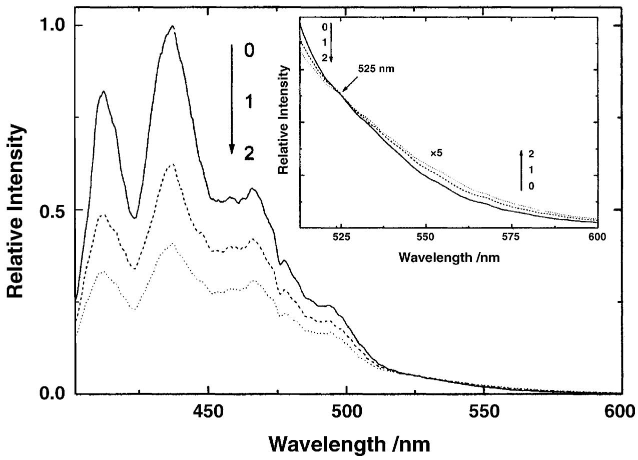

Fig. 8. Steady-state fluorescence emission spectra ($\lambda_{ex} = 403$ nm), in THF fluid solution, of 9CNA (conc. $\sim 1.63 \times 10^{-5}$ mol dm^{-3}) with different concentrations (mol dm^{-3}) of 9PC in (0) 0: (1) 5.43×10^{-3}; (2) 1.61×10^{-2}, at 296 K. *Inset*: Representation of the same spectra in the wavelength region 500–600 nm.

sponding spectra of 9CNA and the exciplex which is hidden within the fluorescence band envelop of 9CNA.

Thus, an attempt was made in the present investigation to see directly the exciplex which seems to be hidden within 9CNA fluorescence in NH. Using THF solvent as the medium whose polarity is higher ($\epsilon_s \sim 7.6$) than that of NH, the quenching studies were made on the fluorescence of 9CNA with the addition of 9PC. Interestingly a broad band appears at 550–600 nm region with an isoemissive point at around 525 nm (inset of Fig. 8). Thus, it is seen that with increase of the polarity of the environment from NH to THF, there is a large red shift in the position of the isoemissive point (from 462 nm in NH to 525 nm in THF). This observation corroborates our presumption, made from steady state and time resolved fluorescence spectral analysis, that a radiative exciplex of charge transfer (CT) nature is formed between the excited 9CNA and 9PC in non-polar environment NH and this exciplex due to its CT nature undergoes red shift due to increase of polarity of the environment from NH to THF. The following mechanism may be proposed from the above observations:

$$9\text{CNA}^* + 9\text{PC} \rightleftharpoons {}^1(9\text{CNA}^{\delta-} \cdots 9\text{PC}^{\delta+})^* \xrightarrow{h\nu} 9\text{CNA} + \text{PC}$$

The presence of isoemissive point (Fig. 8) indicates that the excited reacting species (9CNA* monomer) and the products (exciplex) are in equilibrium and their relative proportions are controlled by the concentration of 9PC (donor).

3.6. *Transient absorption spectra by laser flash photolysis technique*

Transient absorption spectra of 9CNA in presence of the electron donors PDP and 9PC have been measured by exciting with the third harmonic of Nd:YAG laser to produce S_1 of 9CNA. The measurements were made both in polar ACN and non-polar NH fluid solutions using the different delay times between the exciting and the analyzing pulses. Typical spectra are shown in the Fig. 9a–c. A peak near 430 nm is found in each case.

It was reported earlier [39,40] that in highly polar ACN medium 9CNA exhibits only the 430 nm band which should be assigned as the mixture of the triplet–triplet (T–T) absorption of pure 9CNA whose decay time is 560 μs and the cationic species of this molecule having lifetime of ~2 μs. However, in most cases the transient absorption decay at 430 nm for only 9CNA in ACN was found to be single exponential and the lifetime from the decay analysis showed only the shorter component (~2 μs), i.e., the component due to the cationic species. According to Zimmermann et al. [39] the absorption band of the radical cation of 9CNA ($9\text{CNA}^{\bullet+}$) resides energetically very close (large overlapping) to the corresponding band of pure (monomer) 9CNA whose triplet lifetime is ~560 μs. The cationic species of 9CNA is generated due to electron transfer from singlet excited 9CNA to ACN. As the triplet quantum yield, ϕ_T, of the pure 9CNA in ACN is very small (~0.021) [39], the cationic band intensity masks significantly the absorption band of 9CNA. Due to this, only cationic lifetime (~2 μs) appears to be present. However, following the ideas of Zimmermann et al. [39], the two possibilities in the case of 9CNA could be considered. In 9CNA/ACN system the charge separation may occur from singlet excited 9CNA to the solvent or the excited 9CNA could capture electron from the solvent as shown below:

$$9\text{CNA}^* + \text{ACN} \longrightarrow 9\text{CNA}^+ + \text{ACN}^- \qquad \text{(a)}$$

$$9\text{CNA}^* + \text{ACN} \longrightarrow 9\text{CNA}^- + \text{ACN}^+ \qquad \text{(b)}$$

As the energy balance yields $\Delta G^0 = +0.34$ eV for (a) and $\Delta G^0 = +2.6$ eV for (b), it was concluded by Zimmermann et al. [39] that formations of radical cation of 9CNA ($9\text{CNA}^{\bullet+}$) is more favorable than radical anion ($9\text{CNA}^{\bullet-}$). This proposition is quite in agreement with the experimentally observed decay (~2 μs) at 430 nm. Nevertheless, in the present investigation the situation differs when PDP (or 9PC) is added to ACN solution of 9CNA. Apart from the 430 nm band, which is only observed when 9CNA is present in ACN, the additional bands at around 490–570 nm develop in presence of the donors (PDP and 9PC). The decay at 430 nm becomes biexponential (Fig. 10) and the yielded lifetimes were found to be 1.2 μs and 560 μs associated with fractional contributions 0.18 and 0.82, respectively. These observations seem to indicate that the triplet of 9CNA becomes somehow populated. Following the observations made earlier [41] the band at 570 nm region of the transient absorption spectra of 9CNA* + PDP and 9CNA* + 9PC systems in ACN medium (Fig. 9a and b) should be assigned to the band of 9CNA radical anion ($9\text{CNA}^{\bullet-}$) or the mixture of contact ion-pair and solvent-separated ion-pair. It is to be pointed out in this connection that the PDP cation ($\text{PDP}^{\bullet+}$) could not be observed in the present investigation as it absorbs in the region of 780 nm

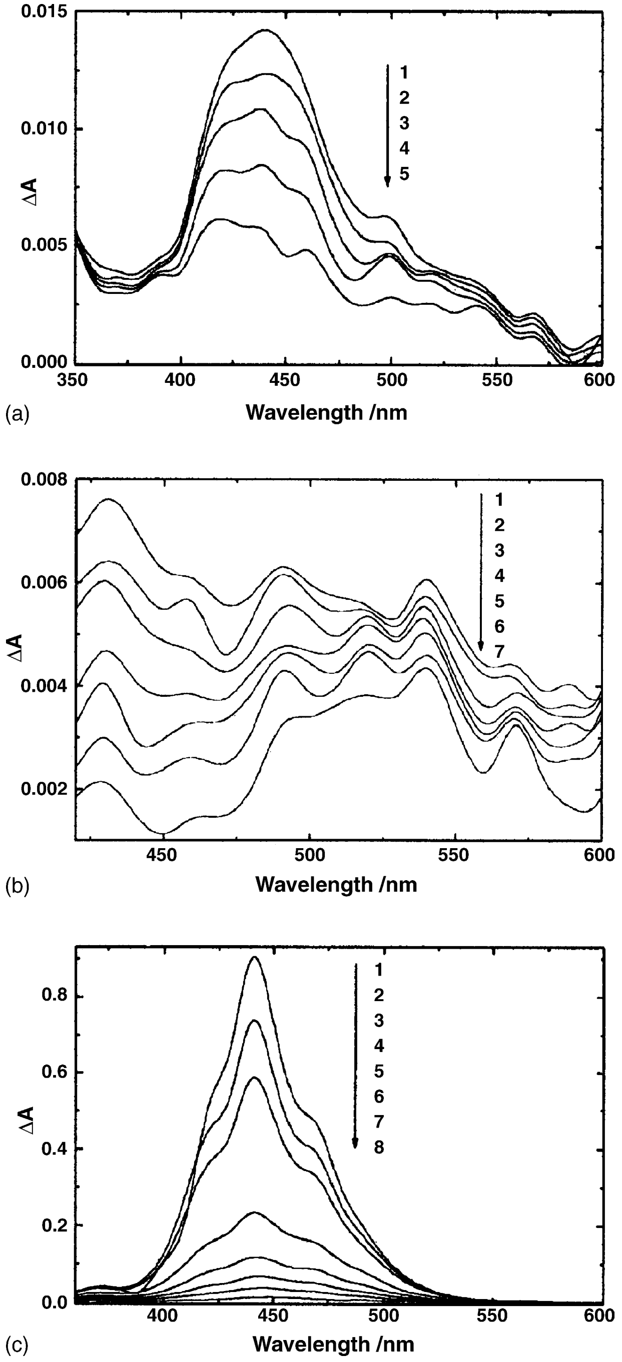

Fig. 9. Transient absorption spectra ($\lambda_{ex} \sim 355$ nm), at the ambient temperature of (a) 9CNA (conc. $\sim 4.44 \times 10^{-5}$ mol dm^{-3}), in ACN, in the presence of the donor PDP (conc. $\sim 1.95 \times 10^{-2}$ mol dm^{-3}) at the different delay times (μs): (1) 2.0; (2) 2.2; (3) 2.5; (4) 3.0; (5) 4.0, (b) 9CNA (conc. $\sim 4.44 \times 10^{-5}$ mol dm^{-3}), in ACN, in the presence of the donor 9PC (conc. $\sim 2.0 \times 10^{-2}$ mol dm^{-3}) at the different delay times (μs): (1) 1.82; (2) 1.94; (3) 2.2; (4) 2.5; (5) 2.9; (6) 3.4; (7) 4.5, (c) 9CNA (conc. $\sim 3.84 \times 10^{-5}$ mol dm^{-3}), in NH, in presence of the donor 9PC (conc. $\sim 1.05 \times 10^{-2}$ mol dm^{-3}) at the different delay times (μs): (1) 0.8; (2) 0.9; (3) 1.0; (4) 1.5; (5) 2.0; (6) 2.5; (7) 3.0; (8) 4.0.

which was beyond the wavelength range available with the present apparatus. In the case of the 9CNA* + PDP system, the 570 nm band was too weak to measure decay (Fig. 9a). So the analysis was made only on the prominent decay observed at the same energy position for the other, 9CNA* + 9PC, system (Fig. 9b).

Charge recombination (CR) within geminate ion pairs (GIPs) proceeds through two types of intermediates: contact ion pairs (CIPs) and sovent-separated or loose ion pairs (SSIPs) [42–45]. According to direct investigations, the involvement of SSIPs in CR is characterized by a biexponential decay of the GIP population, with the faster decay corresponding to the CIP and the slower one to the SSIP [46–48] because in the latter case recombination occurs due to the close approach of the donor and acceptor molecules by slow diffusion process. In the present case, the decay of the GIP population, measured at 570 nm (Fig. 11), was found to be biexponential in nature, with the rate constants (reciprocal of the lifetimes) 4.17 μs^{-1} and 0.71 μs^{-1}. The faster component is due to CR within CIPs ($\tau \sim 0.24$μs) and the slower one corresponds to CR through SSIPs (1.4μs).

The transient absorption decay at 540 nm is single exponential (Fig. 12) and the lifetime estimated from the decay is ~1 μs. This value is very close to the magnitude of the lifetime of the slower component (~1.4μs) observed from the analysis of 570 nm decay. It appears that the 540 nm band could be assigned to the band of the 9CNA anion radical (9CNA$^{\bullet -}$) of loose structured solvent separated ion-pair (SSIP) species where charge-recombination would be slower relative to the process involved within CIP where recombination decay time was found to be 0.24 μs, as discussed above.

In ACN the triplet population of 9CNA, as apparent from the analysis of 430 nm decays (discussed above) of 9CNA*

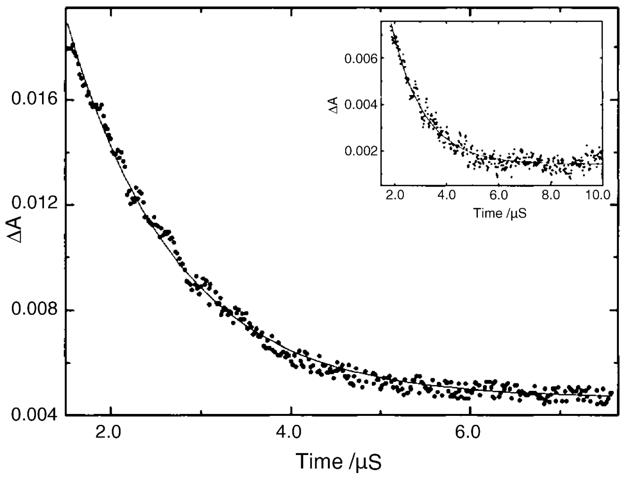

Fig. 10. The time profile of the absorbance (Δ*A*), in ACN, of the transient species at 430 nm in the mixture of 9CNA (conc. $\sim 4.44 \times 10^{-5}$ mol dm^{-3}) and PDP (conc. $\sim 1.95 \times 10^{-2}$ mol dm^{-3}). The decay kinetic analysis yields lifetimes of ~1.2 and ~560 μs. *Inset*: The time profile of the absorbance (Δ*A*), in ACN, of the transient species at 430 nm in the mixture of 9CNA (conc. $\sim 4.44 \times 10^{-5}$ mol dm^{-3}) and 9PC (conc. $\sim 2.0 \times 10^{-2}$ mol dm^{-3}).

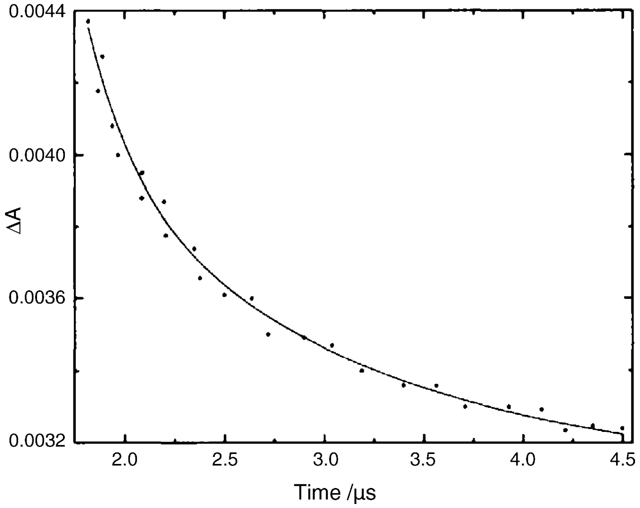

Fig. 11. The time profile of absorbance (ΔA) in ACN, of the transient species at 570 nm in the mixture of 9CNA (conc. $\sim 4.44 \times 10^{-5}$ mol dm^{-3}) and 9PC (conc. $\sim 2.0 \times 10^{-2}$ mol dm^{-3}). The decay analysis shows two species with lifetimes ~0.24 and 1.4 µs.

+ PDP and 9CNA* + 9PC systems, seems to occur from charge recombination mechanism.

The Gibbs free energy changes in ACN for back electron transfer (charge recombination) reactions to form excited triplet, $\Delta G_\mathrm{b}(T)$ and ground state, $\Delta G_\mathrm{b}(G)$ of the fluorescer (acceptor 9CNA) were computed from Eqs. (5 and 6) [49,50]:

$$\Delta G_\mathrm{b}(G) = -E_{1/2}^{\mathrm{OX}}(D/D^+) + E_{1/2}^{\mathrm{RED}}(A^-/A) \qquad (5)$$

$$\Delta G_\mathrm{b}(T) = E_{1/2}^{\mathrm{RED}}(A^-/A) - E_{1/2}^{\mathrm{OX}}(D/D^+) + E_\mathrm{T}^* \qquad (6)$$

The computed values of $\Delta G_\mathrm{b}(G)$ and $\Delta G_\mathrm{b}(T)$ were found to be −2.414 and −0.61 eV (for 9PC–9CNA*) and −2.52 and −0.72 eV (for PDP–9CNA* system), respectively.

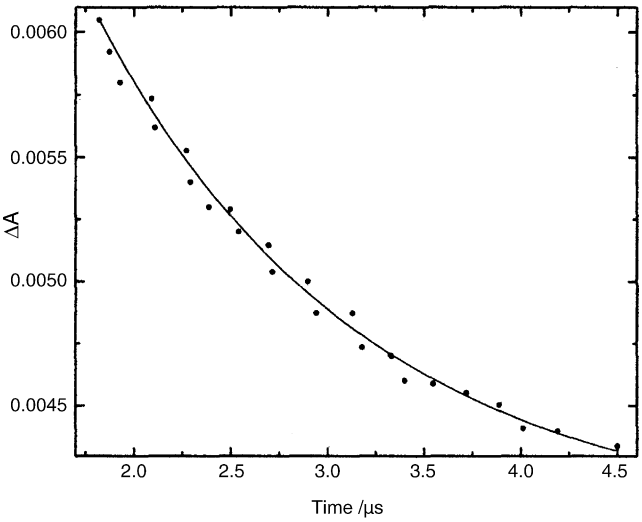

Fig. 12. Single exponential fitting of the transient absorption decay, at 540 nm, in the mixture of 9CNA (conc. $\sim 4.44 \times 10^{-5}$ mol dm^{-3}) and 9PC (conc. $\sim 2.0 \times 10^{-2}$ mol dm^{-3}) in ACN.

As both the parameters are negative, there are possibilities, from thermodynamic point of view, of formations of both the ground state and the excited triplet (T_1) state of 9CNA from charge recombination reactions. The observed large increase in fractional contribution of 560 µs component relative to that of the shorter one in the decay of 9CNA in presence of the quencher PDP (or 9PC) is in accord to this presumption made from thermodynamical consideration.

In the transient absorption of 9CNA, another band at 490 nm develops both in the presence of PDP and 9PC in ACN, which gradually decays with increase of delay times between the exciting and probing pulses. Following the observations made earlier by Ganguly and Burkhart [9] this band was initially thought to be due to formation of triplet excimer of PDP (possibly triplet excimer of 9PC absorbs at the same energy position). Earlier authors have discussed possibilities of formations of triplet excimers of PDP in solutions [15]. It is logical to presume that ion-pair recombination may also produce PDP triplets along with the triplets of 9CNA. The ion recombination in fluid solution has the effect of placing a triplet-state PDP molecule (T_m) in the immediate vicinity of a ground state molecule (M_0) enhancing the possibility of triplet excimer ($^3E^*$) formation.

$$T_\mathrm{m} + M_0 \longrightarrow {}^3E^*$$

Nevertheless, to obtain conclusive evidence of the formation of triplet excimer, the transient decays at 490 nm (Fig. 13) of both PDP + 9CNA* and 9PC + 9CNA* systems were measured. The values were very similar (~1.5 µs) and much lower than the observed lifetimes of triplet excimer of PDP (or 9PC) (~100 µs) [9]. Moreover, $\Delta G^0(T)$ value of formation of triplet PDP or 9PC was estimated from Eq. (6). The value was found to be ~+0.4 eV. This observation suggests that the thermodynamical possibility of formation of triplet excimer of PDP (or 9PC) via charge recombination process is very slim. The transient decay analysis, as discussed above, confirms the proposition made from thermodynamical considerations. Thus, the 490 nm band could not be assigned to the band of triplet excimer of PDP. Rather it would be more logical to presume that this band may be due to the anionic band of loose ion-pair as its decay time is very similar (~1.5 µs) to that observed from the 540 nm band which is due to anionic band of 9CNA acceptor.

In non-polar NH medium and in the presence of PDP or 9PC, 9CNA exhibits no additional bands in the transient absorption spectrum apart from the 430 nm one (Fig. 9c), unlike the situations observed in ACN environment. On analyzing the transient absorption decay at 430 nm, a single exponential decay with a lifetime of only 2 µs was found. Thus, it is apparent that no additional triplet formation occurs in such non-polar medium in presence of PDP and 9PC. The opposite situation was noticed in polar ACN from the decay analysis, which has been discussed above. From this observation in NH coupled with the absence of anionic band at around 540–570 nm, one could rule out the possibility of oc-

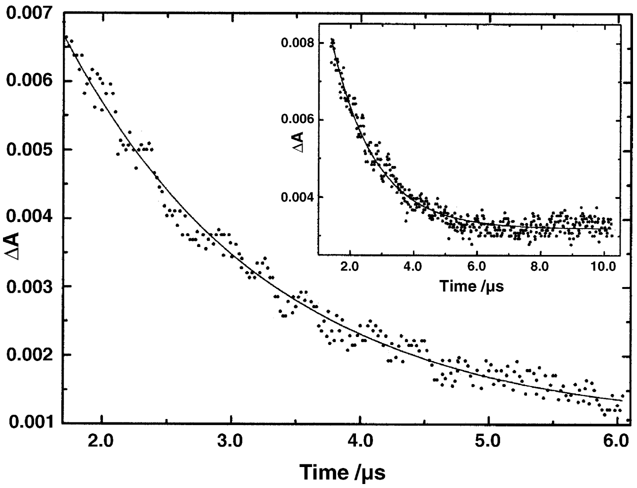

Fig. 13. The time profile of absorbance (ΔA) in ACN, of the transient species at 490 nm in the mixture of 9CNA (conc. $\sim 4.44 \times 10^{-5}$ mol dm^{-3}) and PDP (conc. $\sim 1.95 \times 10^{-2}$ mol dm^{-3}). *Inset*: The time profile of absorbance (ΔA), in ACN, of the transient species at 490 nm in the mixture of 9CNA (conc. $\sim 4.44 \times 10^{-5}$ mol dm^{-3}) and 9PC (conc. $\sim 2.0 \times 10^{-2}$ mol dm^{-3}).

currence of photoinduced ET reactions in the triplet state and so the triplet population through ion-pair recombination is not possible here.

The above findings corroborate our propositions made from steady state and fluorescence lifetime measurements on 9CNA* + 9PC system where in NH medium, the quenching was ascribed due to formation of radiative singlet exciplex (partial charge separated complex). As the lifetime of the exciplex was determined to be ~18 ns, it would decay out, possibly by ion-recombination mechanism, within the nanosecond time interval. This is possibly the reason for the non-observability of ionic species in the transient spectra measured in NH using microsecond delays. This also provides the information of lack of formation of triplet exciplex within the excited acceptor and ground 9PC in such nonpolar medium though from the present investigation formation of singlet exciplex was inferred within the same reacting species.

The observed lack of ion-pair transient bands of 9CNA* + PDP system in NH seemingly indicates the involvements of, not intersystem crossing which generally populates the triplet state, some other channels, through which very fast non-radiative depletion of singlet state of the intermediate exciplex $^1(\text{9CNA}^{\delta-} \cdots \text{PDP}^{\delta+})^*$ occurs.

4. Concluding remarks

Both steady state and time resolved spectroscopic measurements coupled with electrochemical investigations demonstrate the formations of ion-pair species through photoinduced ET reactions between excited 9CNA and 9PC or PDP in polar ACN medium both in the excited singlet and triplet states. In non-polar NH, though formation of radiative exciplex through partial charge separation reactions within 9CNA and 9PC in the excited singlet state was apparent, it seems exciplex of non-radiative nature is formed when PDP, where heavy atom “phosphorus” is present as heteroatom, interacts with the excited 9CNA. In NH the absence of transient ion-pair bands suggests in favor of non-occurrence of photoinduced ET reactions with the present donor–acceptor systems in the triplet state. Lack of involvement of intersystem crossing channel to depopulate the singlet exciplexes formed with the donor–acceptor systems seems to be responsible for this phenomenon.

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