

Investigations on the Photoreactions of Phenothiazine and Phenoxazine in Presence of 9-cyanoanthracene by Using Steady State and Time Resolved Spectroscopic Techniques

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Abstract By using electrochemical, steady state and time resolved (fluorescence lifetime and transient absorption) spectroscopic techniques, detailed investigations were made to reveal the mechanisms of charge separation or forward electron transfer reactions within the electron donor phenothiazine (**PTZH**) or phenoxazine (**PXZH**) and well known electron acceptor 9-cyanoanthracene (**CNA**). The transient absorption spectra suggest that the charge separated species formed in the excited singlet state resulted from intermolecular photoinduced electron transfer reactions within the donor **PTZH** (or **PXZH**) and **CNA** acceptor relaxes to the corresponding triplet state. Though alternative mechanisms of via formations of contact neutral radical by H-transfer reaction have been proposed but the observed results obtained from the time resolved measurements indicate that the regeneration of ground state reactants is primarily responsible due to direct recombination of triplet contact ion-pair (CIP) or solvent-separated ion-pair (SSIP).

Keywords Time resolved spectroscopy · Contact ion-pair · Neutral radical · H-transfer · Fluorescence quenching · Laser flash photolysis · Electron transfer

Introduction

Photoinduced electron transfer (PET) has been an interesting as well as attractive area for several decades [1–12]. Among different cation dyes, **PXZH** and **PTZH** have been extensively used as electron transfer mediators for enzymatic redox reactions and biosensor development [13–17]. As both **PTZH** and **PXZH** are low-potential reductant [18], they possess a spectroscopically well-characterized one-electron oxidized product, **PTZ⁺**, **PXZ⁺** [19, 20]. Hence these molecules have been used as redox probe to study photoinduced charge-transfer reactions [18, 20, 21]. Moreover **PTZH** and **PXZH** are widely used for understanding different mechanisms involved in a DNA mediated charge transfer reactions. The mechanisms include hole transfer process, single-step superexchange, multistep hopping, phonon assisted polaron hopping, and ion-gated hopping in DNA [22–30]. The electron donating property (due to eight ($\pi+n$)-electrons in the central ring) [31] of both the **PTZH** and **PXZH** derivatives, makes them potentially applicable as electroluminescent and photovoltaic cells [31–35]. This potential application of **PTZH** and **PXZH** attracts a great interest of materials science.

For better understandings of these two important donors, photophysical and photochemical studies on **PTZH** and **PXZH** still remain as a very active field of research. In the present investigations, **PTZH** and **PXZH** act as electron donors and 9 cyanoanthracene (**CNA**) as electron acceptor. Systematic steady state and time resolved spectroscopic studies were made on the PET reactions between these two donors **PXZH** or **PTZH** and acceptor **CNA** respectively. It was found that in highly polar medium acetonitrile (ACN), the major non-radiative pathway seems to be due to photoinduced electron transfer (PET). Detailed studies were made by using electrochemical, steady state and time

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resolved (fluorescence lifetime and transient absorption) spectroscopic techniques to reveal the mechanisms of charge separation or electron transfer reactions within the **PTZH** or **PXZH** and well known electron acceptor **CNA** (Chart 1). All the results obtained from the present experimental investigations seemingly indicate that here fluorescence quenching is due to rapid outer sphere electron transfer (ET) as it occurs in the intermediate region ($-0.4 \text{ eV} > \Delta G_{CS} \geq -2.0 \text{ eV}$) and of purely dynamic in nature. It is to be pointed out in this connection that in bimolecular forward ET reactions the rate constant associated with this process generally increases with increase of the ET driving force ($-\Delta G_{CS}$) i.e., with exergonicity upto a diffusion-limited value. The region near diffusion-limited value is known as intermediate region. Marcus theory predicts that [36] beyond intermediate region, with further increase of exergonicity (more negative value of ΔG_{CS}) the ET rate constant decreases. This region is called the Marcus inverted region (mir).

Moreover from the transient absorption spectral measurements attempts were made to reveal the mechanism of the regeneration of ground state reactants, whether through direct recombination mechanism of the triplet contact ion-pair (CIP) or triplet solvent separated ion-pair (SSIP) or alternatively via formations of contact neutral radical by H-transfer. In the present paper the steady state and time resolved spectroscopic results obtained for these **PTZH** and **PXZH** donors especially in presence of the well known acceptor **CNA** and their interpretations are described in details.

Experimental section

Materials

All the samples **PTZH**, **PXZH**, **CNA** (97% pure) (Chart 1) supplied by Aldrich, were purified by crystallization method. The solvent acetonitrile (ACN) (Sisco Research Laboratory) of spectroscopic grade was distilled under vacuum following the standard procedure and tested before

use to detect any impurity emission in the concerned wavelength region.

Spectroscopic apparatus

Steady state UV-vis and fluorescence emission spectra of moderate concentrated solutions (10^{-3} – 10^{-5} M) 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 2101PC) and F-4500 fluorescence spectrophotometer (Hitachi), respectively. Fluorescence lifetime measurements were carried out by the time correlated single photon counting method by using HORIBA JOBIN YVON FLUOROCUBE. The emission was collected at a magic angle polarization using a Hamamatsu MCP photomultiplier (2809U). The time correlated single photon counting (TCSPC) set up consists of an ortec 9327 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. The channel width is 12 ps / channel. The fluorescence decays were deconvoluted using IBH DAS6 software. The quality of fit was assessed over the entire decay, including the rising edge, and tested with a plot of weighted residuals and other statistical parameters e.g. the reduced χ^2 and the Durbin-Watson (DW) parameters. All the solutions for room temperature measurements were deoxygenated by purging with argon gas stream for about 30 min.

Laser flash photolysis (LFP)

The experiments were carried out in a conventional LFP set-up (laser kinetic spectrometer, Applied Photophysics). In the present work of LFP studies third harmonic (355 nm) of a Nd:YAG (DCR-11, Spectra Physics) laser as a pump source, and a 250 W pulsed xenon lamp as the monitoring source have been used. The output signal from the photomultiplier (1P28) was fed to a digital storage oscilloscope (Tektronix, TPS2012) and the data was transferred to a computer using TekVISA software. The time resolution of the instrument is 7–8 ns (pulse width).

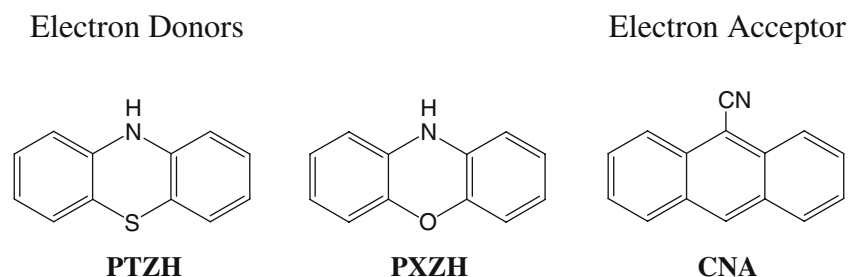


Chart 1 Molecular structures of the compounds **PTZH**, **PXZH** and **CNA**

Electrochemical measurements

Electrochemical measurements were performed at 298 K under a dry nitrogen atmosphere on a PC-controlled PAR model 273A electrochemistry system. A platinum disk (working) electrode, a platinum wire (auxiliary) electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. The $E_{1/2}$ for the ferrocenium-ferrocene couple under our experimental condition was 0.39 V. Voltage sweep rate was 50 mV/s. Tetraethylammonium perchlorate (TEAP) in ACN (~ 0.1 M) was used as a supporting electrolyte.

Results and discussion

Electron transfer (ET) thermodynamics

The one electron oxidation potential (E^{OX}) of the donor **PTZH** or **PXZH** and the one-electron reduction potential (E^{RED}) of the well known electron acceptor **CNA** were measured by the cyclic voltammogram in ACN medium (details of the measurements are given in the experimental section). The values of the redox potentials are shown in Table 1. The singlet excitation energy value (${}^1E^*$) of **CNA** was determined from the average of absorption maximum and fluorescence maximum. This value was estimated to be 3.03 eV.

By using the expression (1), the values of free energy changes (ΔG_{CS}) of PET from ground **PTZH** (or **PXZH**) to excited singlet state (S_1) of **CNA** acceptor were computed using the experimentally observed values of E^{OX} of the donor and E^{RED} of the acceptor.

$$\Delta G_{CS} = e(E^{OX} - E^{RED}) - {}^1E^* \quad (1)$$

In the above expression the electrostatic stabilization term has been neglected as in highly polar solvent like

Table 1 Values of redox potentials, ${}^1E^*$, driving force for photoinduced charge separation reaction (ΔG_{CS}) within the donors **PTZH**, **PXZH** and the acceptor **9CNA** molecules in ACN solvent at the ambient temperature

Donor	Acceptor	E^{OX} V	E^{RED} V	${}^1E^a$ eV	ΔG_{CS} eV
PTZH (or PXZH) ^b	CNA	+0.6	-1.13	-	+1.73
PTZH (or PXZH) ^b	CNA ^a	+0.6	-1.13	3.03	-1.30

^a denotes the excited singlet state S_1

^b as E^{OX} value of **PXZH** was found very similar ($\sim +0.6$ V), from electrochemical measurements, as that of the other donor **PTZH**, the equal magnitude of ΔG_{CS} of both the donors when they interact with excited (S_1) acceptor **CNA** was found.

ACN its contribution is as low as 0.06 eV which could be neglected.

The ΔG_{CS} values for **PTZH-CNA*** (* denotes the excited singlet state) and **PXZH-CNA*** determined from the expression (1) have been listed in Table 1. As magnitudes of E^{OX} values of **PTZH** and **PXZH** are very similar to each other, same ΔG_{CS} values (~ -1.3 eV) are obtained for both the donor-acceptor pairs studied in the present investigation.

The free energy changes of back electron transfer (charge recombination) reactions for the present donor-acceptor pairs were estimated from the expression:

$$\Delta G_{CR} = -e[E^{OX} - E^{RED}] \quad (2)$$

and the value was found to be -1.73 eV.

Following Kikuchi [37] it is apparent from the observed values of ΔG_{CS} and ΔG_{CR} that the photoinduced charge separation reactions within ground state donor (**PTZH** or **PXZH**) and excited singlet acceptor **CNA** occur in the intermediate region within the framework of the Marcus theory [36] and the charge recombination or back electron transfer proceeds also through the same region as in both cases the values of free energy changes are >-2.0 eV.

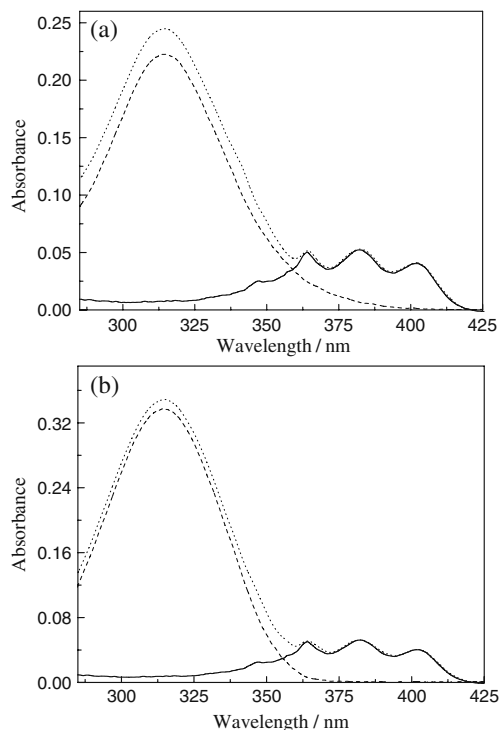


Fig. 1 (a) Steady state UV-vis absorption spectra of **CNA** (solid line) (Conc. $\sim 1 \times 10^{-5}$ M), **PTZH** (dashed line) (Conc. $\sim 5 \times 10^{-5}$ M), and mixture of **PTZH** and **CNA** (dotted line) in ACN; (b) Steady state UV-vis absorption spectra of **CNA** (solid line) (Conc. $\sim 1 \times 10^{-5}$ M), **PXZH** (dashed line) (Conc. $\sim 5 \times 10^{-5}$ M), and mixture of **PTZH** and **CNA** (dotted line) in ACN

From the observed (Table 1) positive values of ΔG_{CS} , when unexcited donor and acceptor interact with each other, possibility of occurrence of charge-transfer reactions is very slim. From the thermodynamic point of view the occurrence of charge-separation reaction appears to be possible only when one of the reacting species is excited as shown from the negative values of ΔG_{CS} (Table 1).

UV-vis, steady state spectroscopic and time resolved fluorescence measurements

In ACN medium, the UV-vis absorption spectra of the mixture of PTZH (or PXZH) and CNA are observed to be the superposition of the corresponding spectra of both the reacting species (Fig. 1a and b). This indicates the lack of formation of any ground state of electron donor-acceptor complex under the present experimental conditions.

However, the steady state fluorescence emission intensity of the acceptor CNA (produced by exciting the 402 nm

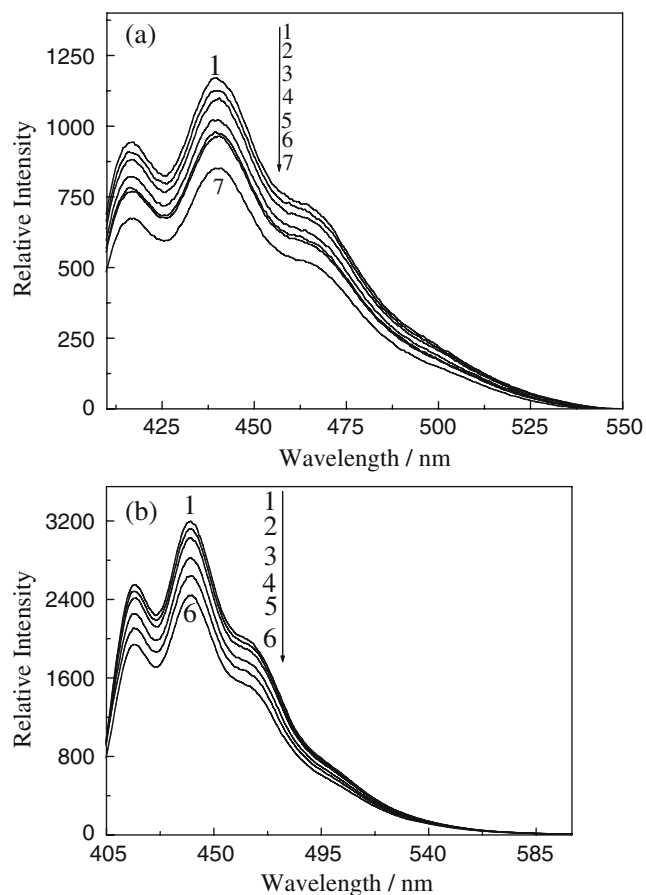


Fig. 2 (a) Fluorescence emission spectra of CNA (Conc. $\sim 1 \times 10^{-5}$ M) with excitation ~ 402 nm in presence of different conc. of PTZH: (1) 0 M, (2) 10^{-4} M, (3) 2×10^{-4} M, (4) 4×10^{-4} M, (5) 6×10^{-4} M, (6) 8×10^{-4} M, (7) 1×10^{-3} M. (b) Fluorescence emission spectra of CNA (Conc. $\sim 1 \times 10^{-5}$ M) with excitation ~ 402 nm in presence of different conc. of PXZH: (1) 0 M, (2) 1×10^{-4} M, (3) 3×10^{-4} M, (4) 5×10^{-4} M, (5) 7×10^{-4} M, (6) 1×10^{-3} M

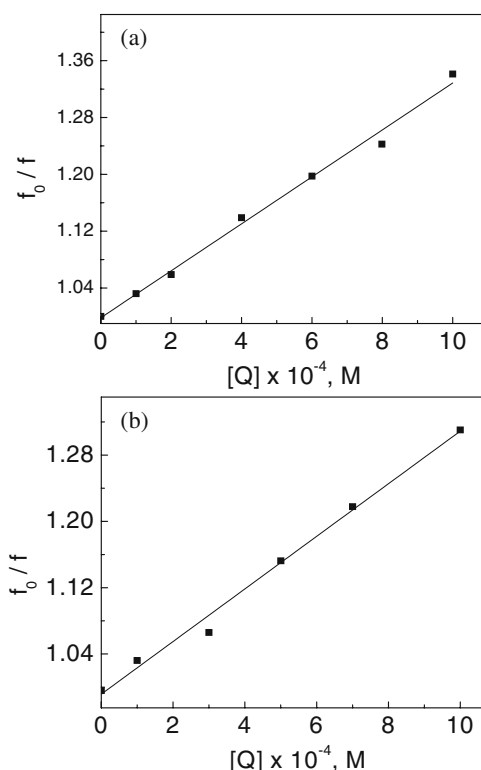


Fig. 3 (a) SV plot of mixture of CNA and PTZH. (b) SV plot of mixture of CNA and PXZH

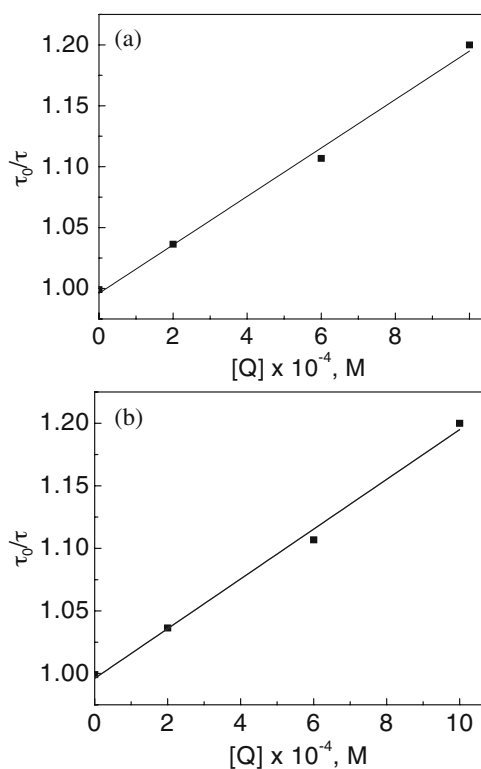


Fig. 4 (a) Stern –Volmer (SV) plot from fluorescence lifetime measurements (time resolved) of mixture of CNA and PTZH. (b) Stern –Volmer (SV) plot from fluorescence lifetime measurements (time resolved) of mixture of CNA and PXZH

wavelength where the donor **PTZH** or **PXZH** is transparent) is quenched regularly throughout the entire band envelop with gradual addition of the donor **PTZH** or **PXZH** (Fig. 2a and b).

As the fluorescence quenching of **CNA** occurs in the region of the donor concentrations where the absorption spectra of **CNA** remains unaffected, to analyze the fluorescence quenching data for revealing the mechanisms of PET within the present donor-acceptor systems simple Stern-Volmer (SV) relation (3) [38–42] could be used:

$$f_0/f = 1 + k_q\tau_0[Q] \quad (3)$$

where f_0 and f are the fluorescence intensities of the fluorophore **CNA** in the absence and presence of the quencher (the donors) respectively and τ_0 is the fluorescence lifetime of the free **CNA**. k_q is the bimolecular quenching rate constant and $[Q]$ is the concentration of the quencher.

The observed linearity in SV plots (Fig. 3a and b) suggests that the quenching may be of either pure dynamic or static in nature [38]. Generally deviations from linearity indicate the mixing of both dynamic and static quenching

processes. However, to locate the true nature of the quenching, time resolved fluorescence measurements were made. It was observed from the measurements of the fluorescence decay of the acceptor **CNA** in **ACN** in presence of the different concentrations of the donor **PTZH** or **PXZH**, the fluorescence lifetime of **CNA** is significantly shortened with gradual addition of the donor as compared with that in the absence. Moreover, the bimolecular quenching rate k_q obtained from the linear plot of f_0/f ($\sim 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for **PTZH-CNA*** and $1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for **PXZH-CNA***) vs various concentration of the quencher **PTZH** or **PXZH** is found to be in good agreement within the experimental error ($\pm 20\%$) with the bimolecular quenching rate values determined from the linear SV plot of τ_0/τ vs quencher concentrations (Fig. 4a and b) ($\sim 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for **PTZH-CNA*** and $2.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ for **PXZH-CNA***). As $f_0/f \approx \tau_0/\tau$ for a concentration of the quencher and rates of ET process as derived from both the SV plots constructed from steady state and time resolved fluorescence are nearly the same, the quenching observed should be of dynamic in nature as reported by earlier authors [40, 42]. Lack of formation of ground state donor-

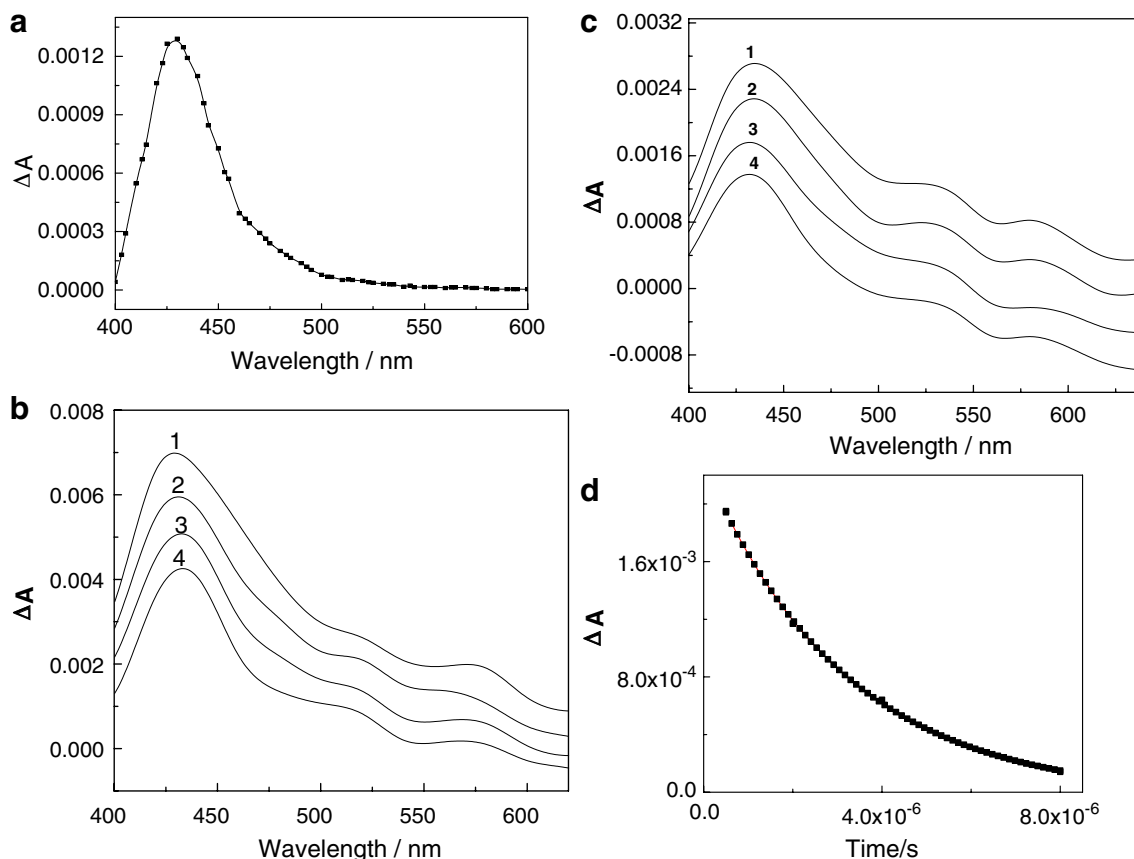


Fig. 5 Transient absorption spectra of (a) **CNA** (only 0.5 μs delay is shown), (b) **CNA+PTZH** and (c) **CNA+PXZH** at delay times: (1) 0.5 μs; (2) 2 μs; (3) 4 μs; (4) 8 μs; measured in **ACN** at the ambient

temperature. (d) Transient decay profile at 575 nm of **CNA+PTZH** system (similar type of decay was also observed for **CNA+PXZH**)

acceptor complex, as evidenced from UV-vis spectral measurements, corroborate our views in favor of involvement of dynamic process in quenching mechanism and absence of static mode. In high probability the photoinduced electron transfer plays a major role in the quenching mechanisms as the possibility of occurrences of another dynamic process excitation energy transfer is very slim since the acceptor having lower lying excited singlet than that of the donor is excited. The direct evidence of occurrence of PET process is provided from the observations of transient donor cationic and acceptor anionic species from the nanosecond laser flash photolysis measurements which have been described below in “Electrochemical measurements”.

As predicted by Kikuchi [37] for the k_q values which are observed to be close to the diffusion-controlled limit, the quenching observed in this investigation appears to be due to rapid outer-sphere electron transfer as it occurs in the intermediate region ($-0.4 \text{ eV} > \Delta G_{CS} \geq -2.0 \text{ eV}$).

Transient absorption measurements by nanosecond laser flash photolysis (LFP) technique

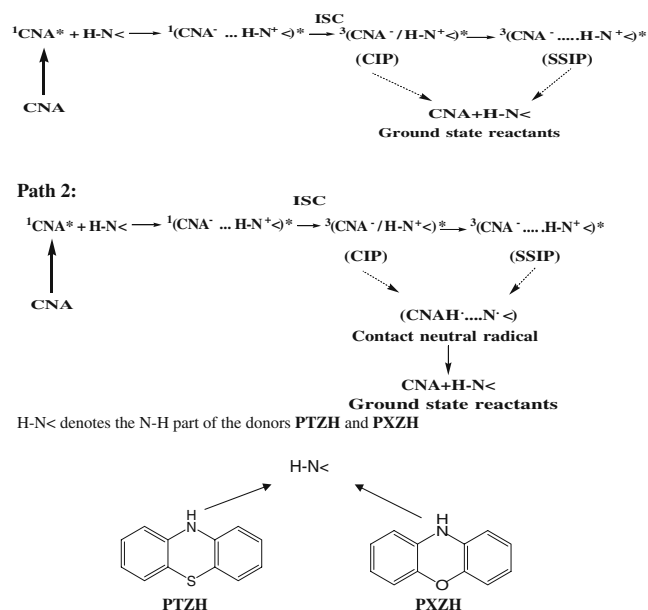
The transient absorption spectra of **CNA** in ACN medium have been measured by using nanosecond laser flash photolysis method by exciting the third harmonic of Nd:YAG laser system (355 nm). The typical spectra are shown in Fig. 5a. The maximum concentrations of **PTZH** and **PXZH** in the mixture with **CNA** had been taken in such a way that the absorptions of **PTZH** and **PXZH** were transparent at 355 nm position at these concentrations. The transient spectra of **CNA** shows a band envelop from 400 nm to 450 nm, peaking at about 430 nm. As reported by Zimmermann et al. [43], this band is mainly due to radical cation of **CNA** because though triplet-triplet (T-T) absorption of **CNA** also resides close to this 430 nm band but due to its low quantum yield (~ 0.021) it contributes marginally to this band. However, the decay of 430 nm band, on analyzing, yields a lifetime of 5.7 μs . Even on using the double exponential fit, to this decay the observed triplet lifetime of pure **CNA** of around 556 μs [44] is not found. It is known that 556 μs is the triplet lifetime of pure **CNA** in ACN. Thus, as reported by Zimmermann, this 430 nm band appears to be primarily due to radical cation of **CNA**. The origin of this **CNA** cationic band is not very clear. Nevertheless, from laser flash photolysis experiments, Zimmermann and his group [43] inferred that in ACN the compound **CNA** undergoes monophotonic ionization which results in the formation of cationic species of **CNA**.

With the addition of **PTZH** or **PXZH** a weak band at around 525 nm region (Fig. 5b and c) develops along with another band at 575 nm region. According to the earlier

report [45] the band at 525 nm could be assigned as the band of donor cation PTH^+ and the other one at around 575 nm could be assigned to the anion radical of **CNA** [46].

From the transient spectra of the acceptor **CNA** shown in Fig. 5a–c for various delays, it was clearly observed that additional bands which were absent for only **CNA** (Fig. 5a) develop (Fig. 5b and c) at around 525, 575 nm region in presence of donors **PTZH** or **PXZH**. All these spectra had been recorded in the same experimental conditions and measured several times to confirm the development of these bands at 525, 575 nm in presence of either of the donors used in the present investigations.

As shown in Scheme 1, from the present transient absorption measurements it could be inferred that the charge separated species formed in the excited singlet state (confirmed from the steady state and time resolved fluorescence measurements) relaxes to the corresponding triplet through intersystem crossing (ISC) process. In the present case, it appears that there might be two possible paths which lead to the formations of ground state reactants. Through one of these paths, the productions of the ground state reactants could be formed either by direct recombination of triplet contact ion-pair (CIP) or solvent-separated ion-pair (SSIP) or alternatively via formations of contact neutral radical by H-transfer mechanism. According to Gao et al. [45] the transient absorption band of the free radical PT. of the contact neutral radical was apparent at 390 and 410 nm. But in our case no such peak was obtained at 390 nm. Moreover, one should expect the gradual development of a band at 410 nm at



Scheme 1 Different possible photophysical pathways to regenerate ground state reactants

the expense of the 525 nm band of the cationic species of the donor molecule with increase of delay times, if there is a possibility of formation of contact or solvent-separated neutral radicals by transfer of hydrogen atom from >NH group of the donors (Scheme 1). Actually from the transient spectra of CNA in presence of either of the donors, the gradual decrement of the transient absorption intensity throughout the entire band envelop was observed with increase of the delay times between the exciting and the analyzing pulses (Fig. 5b and c). All these observations demonstrate that the most favorable path for the formation of ground state reactants should be through direct CIP or SSIP recombination mechanism (Path 1, Scheme 1). The lack of evidence for the growth of 410 nm band at the expense of the 525 nm band corresponding to the donor cationic species suggests path 2 (Scheme 1) as less favorable path for production of the ground state reactants via formation of contact neutral radical by H-transfer mechanism. Further, from the decay analysis at 575 nm (position of acceptor anionic species) (Fig. 5d) ion-pair lifetime, τ_{ip} was determined for both the donor-acceptor pairs. Both the lifetimes were found to be close to each other (~ 4 and $7 \mu\text{s}$). The charge recombination rate of the ions (cationic species of the donor and the anionic species of the acceptor), k_{CR} , was computed by using the expression (4), as used by Durocher et al. [47]:

$$k_{CR} = 1/\tau_{ip} - k_{CST} \quad (4)$$

where k_{CST} is the rate associated with formation of loose-structured charge-separated species computed from φ_R / τ_{ip} .

φ_R is the yield of loose-structured charge-separated species calculated from the transient decay as described by Durocher et al. [47].

For both the donor-acceptor systems, the charge recombination rate was found to be of the same order of magnitudes (k_{CR} values are $3.1 \times 10^5 \text{ s}^{-1}$ for CNA+PTZH and for the other system CNA+PXZH the corresponding value is $\sim 1.4 \times 10^5 \text{ s}^{-1}$). The nearly similar magnitudes of the charge recombination rates ($\sim 10^5 \text{ s}^{-1}$) for both donor-acceptor systems along with the lack of formation of 410 nm band in the transient spectra of both the systems further corroborate our presumption about the regeneration of the ground state reactants through only path 1 i.e., by direct recombination the ionic species (Scheme 1). The relatively more pronounced transient absorption spectra of PXZH relative to PTZH (Fig. 5(b) and (c)) may be due to some structural effect arisen for the change of substitution from “S” to “O” though it is apparent from other observations, as discussed above, that in spite of this effect, the recovery of ground state reactants in the photoinduced

electron transfer processes proceeds primarily through path 1 relative to path 2.

Concluding remarks

The present investigations on intermolecular photoinduced electron transfer reactions within the donor PTZH (or PXZH) and 9CNA acceptor indicate that the charge separated species formed in the excited singlet state (confirmed from the steady state and time resolved fluorescence measurements) relaxes to the corresponding triplet through intersystem crossing (ISC) process. Though there are two possible reaction paths for the productions of the ground state reactants, either by direct recombination of triplet contact ion-pair (CIP) or solvent-separated ion-pair (SSIP) or alternatively via formations of contact neutral radical by H-transfer mechanism, the observed results obtained from the time resolved measurements indicate the former path as the most favorable one.

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