Comparative studies on inter- and intramolecular electron transfer processes within 4-methoxybenzo[b]thiophene (4MBT) and *p*-chloroacetophenone (PCA) reacting systems by using steady-state and laser flash photolysis techniques

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Abstract

Methods of synthesis and characterization of the bichromophores (4MBA and 4MBAS) comprising 4-methoxybenzo[b]thiophene (4MBT) as donor and *p*-chloroacetophenone (PCA) as acceptor linked together by an olefinic (unsaturated in the former bichromophore and saturated in the case of the latter one) bridge have been presented in this paper. The photophysics of these bichromophores has been extensively studied both by steady-state and laser flash photolysis techniques. An attempt was made to compare the monomolecular photophysical properties of the bichromophores with the photophysics of the bimolecular systems where its constituent reacting partners (same donor and acceptor molecules as within the bichromophores) being unlinked will react by diffusion-assisted process. Both from the steady-state electronic absorption and fluorescence emission spectra it shows that the bichromophores exhibit charge transfer (CT) complex both in the ground and excited states. This observation demonstrates that mutual orientation between the donor and the acceptor moieties largely facilitates the formation of such complex. In intermolecular interactions it appears that a weak excited singlet (S_1) CT complex of contact nature is formed, whereas in intramolecular systems (bichromophores 4MBA and 4MBAS) relatively stronger excited CT complexes of two types: *cis* (folded) and *trans* (extended) isomers for 4MBA and two conformers (gauche and staggered) for 4MBAS are formed, as evidenced from steady-state and time-resolved measurements. Transient absorption measurements clearly demonstrate the occurrences of photoinduced intermolecular ET reactions, whereas in intramolecular system direct excitation of ground state CT by using the third harmonic (355 nm) of a nanosecond Nd:YAG laser system produce ion-pair (D^+–A^-) state both in the singlet and triplet states. Transient absorption spectral measurements by laser flash photolysis technique reveal that energy wasting charge recombination process within the bichromophore is largely precluded on changing the nature of the spacer from unsaturated to more flexible saturated one. The necessity of incorporating two spacers (cyclophane type) instead of one to enhance the charge separation rate and to minimize the energy wasting recombination process is hinted.

1. Introduction

Lately considerable efforts have been made to reveal the new aspects of the inter- and intramolecular photoinduced electron transfer (ET) processes with organic molecular systems [1–7]. In recent decades specially photoinduced intramolecular ET has become an object of extensive study [8–12]. In cases of flexible linkers like polymethylene spacers which connect the donor and the acceptor moieties, it is believed that ET could occur if these two redox sites are very close to each other, i.e., within van der Waals contact distances [13,14], so that direct overlap between the orbitals of the chromophores becomes responsible for through space interaction. For achieving this orbital overlap it is necessary

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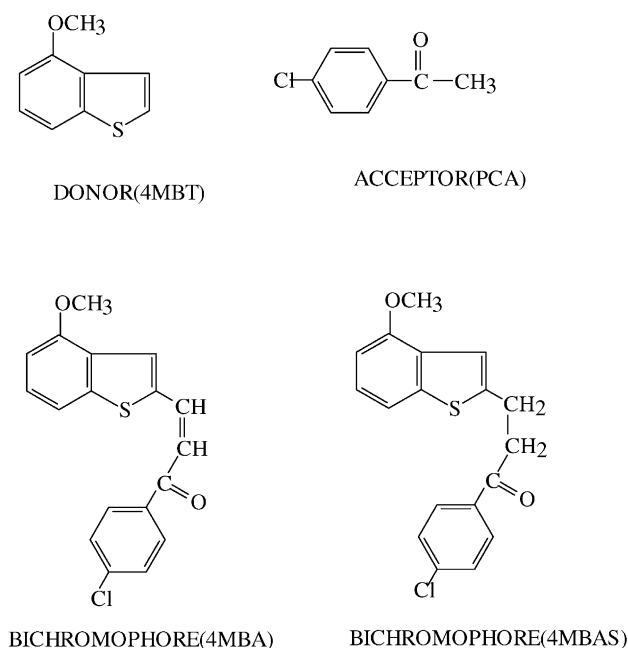*E-mail address:* sptg@mahendra.iacs.res.in (T. Ganguly).

Fig. 1. Molecular structures of 4MBT, PCA, 4MBA and 4MBAS.

that the flexible spacer would be folded. However, occurrence of ET was still observed in some cases [15,16] of rigid systems where the separation distance between the donor and the acceptor is much larger (extended form) than the van der Waals distance. In such circumstances ET reaction is of the nature of through-bond interaction. In this interaction the donor and the acceptor sites interact through their mixing with the π or σ bonds of the linkers. Mutual orientations between the donor and the acceptor sites in linked systems were found to play important role in facilitating ET reactions [17]. Though large amount of work were performed on bichromophoric systems comprising various donor and acceptor moieties connected by spacers of different nature but systematic comparative studies on intermolecular and intramolecular systems using the same donor and acceptor moieties as reacting species are still lacking. This prompts us to undertake this investigation with a synthesized electron donor 4-methoxybenzo[b]thiophene (4MBT) and electron acceptor *p*-chloroacetophenone (PCA) and the newly synthesized bichromophores, 4MBA and 4MBAS (Fig. 1) where the above donor and the acceptor moieties are connected by an olefinic (unsaturated as well as saturated) spacer. Investigations on both intermolecular and intramolecular interactions, measured by steady-state and laser flash photolysis techniques, were made to elucidate the details of the ET reactions occurring in the present linked donor–acceptor systems. An attempt was also made to quantify the charge separation and energy wasting charge recombination processes associated with ET reactions in cases of both inter and intramolecular systems. In the present paper the results from the above studies have been reported and discussed.

2. Experimental

2.1. Materials

The synthesis and characterization of the bichromophores 4MBA and 4MBAS (Fig. 1) have been discussed below in details. The methods of synthesis of the donor 4MBT and its characterization were described elsewhere [6].

2.2. Synthesis of (a) 4MBA and (b) 4MBAS bichromophores

(a) To the well-stirred solution of 4MBT (**1**, 0.5 g, 0.003 mol) in dry THF, 1.5 M *n*-butyl lithium (3 ml, 1.5 equiv.) was added dropwise at −78 °C under inert atmosphere. After stirring the reaction mixture at that temperature for 30 min it was warmed up to −30 °C and again cooled to −78 °C, followed by addition of freshly distilled *N,N*-dimethyl formamide (DMF) (0.438 g, 0.006 mol). After allowing the reaction mixture to attain room temperature and stirring for 12 h at that temperature ammonium chloride solution (10 ml) and water (50 ml), were added followed by extraction with diethyl ether (3 × 25 ml). Washing the organic layer with water drying (anhydrous Na_2SO_4) and evaporation of the solvent afforded the crude material, which purified by column chromatography (ethyl acetate:light petroleum (5:95) as eluent) to obtain **2** as a light yellow crystal. Yield 62%; m.p. 88–90 °C (dichloromethane–light petroleum).

NMR (60 MHz): δ_H 10 (1H, s C*H*O), 8 (1H, s, 3-*H*), 7.5–7.3 (2H, m, 6- and 7-*H*), 6.8 (1H, dd, 5-*H*), 3.9 (3H, s, –OC*H$_3$*).

3(4′-chlorophenyl-3-[4″-methoxy-2-benzo[b]thienyl]-prop-2-ene-1-one).

To the ethanolic solution (65 ml) of **2** and 4-chloro acetophenone (0.3 g, 0.002 mol), 40% KOH solution was added dropwise at 10 °C. The reaction mixture was stirred for 15 min at that temperature and allowed to attain room temperature and stirred overnight. A yellow precipitate appeared and the reaction mixture was acidified with dilute HCl. Upon pouring into 100 ml ice-cold water the separated solid was filtered which was washed with water till free from acid and dried in open air. Compound **3** was obtained as yellow solid, yield: 56%, m.p. 142–144 °C (dichloromethane–light petroleum) NMR (300 MHz, $CDCl_3$): δ_H 8.02 [1H, d, 3-*H* (*trans*), $J = 15$ Hz], 7.98 [1H, d, 3-*H* (*cis*), $J = 5.1$ Hz], 7.97 (2H, d, 2′- and 6′-*H*, $J = 8.4$ Hz), 7.7 (1H, s, 3″-*H*), 7.49 (2H, d, 3′- and 5′-*H*, $J = 8.4$ Hz), 7.48 [1H, d, 2-*H* (*cis*), $J = 5.1$ Hz], 7.4–7.37 (1H, m, 7″-*H*), 7.35 (1H, dd, 6″-*H*, $J = 8.1$ Hz), 7.28 [1H, d, 2-*H* (*trans*), $J = 15$ Hz], 6.75 (1H, dd, 5″-*H*, $J = 7.2$ and 1.2 Hz), 3.97 (3H, s, –OC*H$_3$*).

Analytical calculation for $C_{18}H_{12}O_2SCl$: C, 65.74% and H, 3.98%. Found C, 65.64% and H, 3.89%.

(b) Compound **3** (0.1 g, 3.04 mol) was hydrogenated in the presence of 10% Pd–C (156 mg) in ethyl acetate (10 ml). Uptake of H_2 ceased after 6 h. The mixture was filtered and washed with ethyl acetate. The filtrate was concentrated. The residue was purified by preparative TLC (ethyl acetate:light petroleum (2:98) as eluent) to afford **4** as a colorless liquid. Yield: 50%.

NMR (300 MHz, CDCl₃): δ_H 7.9 (2H, d, 2′ and 6′-*H*, $J = 8.7$ Hz), 7.4 (1H, d, 3′- and 5″-*H*, $J = 8.7$ Hz), 7.3 (1H, d, 7″-*H*, $J = 8.1$ Hz), 7.23 (1H, s, 3″-*H*), 7.2 (1H, dd, 6″-*H*, $J = 7.8$ Hz), 6.7 (1H, dd, 5″-H, $J_{ortho} = 7.8$ Hz), 3.9 (3H, s, –OC*H₃*), 3.4–3.3 (4H, m, –C*H₂*–C*H₂*–).

Analytical calculation for $C_{18}H_{15}SO_2Cl$: C, 65.34% and H, 4.57%. Found C, 65.25% and 4.90%.

2.2.1. Other chemicals used and their purifications

PCA was purchased from Aldrich and distilled by short path distillation before use.

Acetonitrile (ACN), *n*-heptane (NH), ethanol (EtOH), tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) purchased from E. Merck, Germany, of spectroscopic grade, were purified according to standard procedure and tested, before use, for the absence of any impurity emission in the wavelength regions studied.

2.3. Spectroscopic apparatus

At the ambient temperature (296 K) steady-state electronic absorption and emission spectra of dilute solutions ($\sim 10^{-4}$–10^{-6} mol dm^{-3}) of the samples were recorded 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. A special dewar in which a long cylindrical quartz tubing (cell) (3 mm in diameter) could be introduced, was used for low-temperature (77 K) measurements. The excitation wavelength for emission of the electron donor (4MBT) was selected at 307 nm, that of electron acceptor (PCA) at 330 nm and that of 4MBA and 4MBAS at 351 nm positions both at the room and low temperatures.

Picosecond single photon counting techniques: Fluorescence decays of the bichromophore 4MBA having very low lifetime were recorded using single photon counting set-up (Millenia (5W) CW 532 nm pumped Tsunami Ti:sapphire mode-locked laser with pico-option (720–850 nm), SHG and THG as the pump source from Spectra Physics USA) with pulsed width <2 ps with 250 nm excitation. IBH 5000U Fluorescence spectrophotometer used for picosecond excitation and detection system with MCP-PMT:R3809U (160–850 nm), Polarizers, NIM timing electronics and PC-based MCA with utility software and window-based data analysis software (IBH software library). Iterative sift of the fitted function as part of χ^2 (error ±6 ps, standard deviation ±4 ps). N₂/H₂ filled 100 kHz gated lamp is also available for nanosecond measurement as optional.

Another type of picosecond single photon counting set-up was used to measure the fluorescence lifetime of 4MBAS using a coherent synchronously pumped, cavity dumped rhodamine 6G dye laser (702-1) pumped by a coherent CW mode-locked Antares 76-S Nd:YAG laser. Details of the set-up were given elsewhere [6].

Laser flash photolysis: The laser flash photolysis experiments were done, to measure transient absorption spectra, using the third harmonic of a nanosecond Nd:YAG laser system (355 nm) from Quanta Ray (Spectra Physics, GCR-2, Applied Photophysics) with 8 ns pulse width, pulse energy 150 mJ/pulse. The laser was used in a right angled geometry and a 1 cm path length cell was used in the investigation. The signals were detected using a 250 W pulsed xenon lamp, Czerny Tuner monochromator and R-928 PMT. The signals were captured in an Hewlett-Packard 54201A digitizing oscilloscope. All the measurements were done by using deareated solution made by 30 min argon purging in the solution. The kinetic analyses were carried out using the software described elsewhere [18].

Electrochemical measurements were performed with a PAR model 370-4 electrochemistry system incorporating a model 174 A polarographic analyzer, model 175 universal programmer and model RE0074X-Y recorder. Three-electrode systems including SCE were used in the measurements. Tetraethylammonium perchlorate (TEAP) in ACN was used as supporting electrolyte as before [19].

3. Results and discussion

3.1. Determination of the redox potentials of the reacting species, 4MBT and PCA, by using cyclic voltammetry and computation of the driving energy change, ΔG^0

Using Rehm–Weller relation (Eq. (1)) [20,21] the Gibbs free energy change, ΔG^0, associated with radical ion-pair formation, was estimated

$$\Delta G^0 = E_{1/2}^{OX}\left(\frac{D}{D^+}\right) - E_{1/2}^{RED}\left(\frac{A^-}{A}\right) - E_{0,0}^* - \frac{e^2}{4\pi\varepsilon_0\varepsilon_s R} \tag{1}$$

The first two parameters, half-wave oxidation potential of 4MBT and half-wave reduction potential of PCA, were measured in ACN solvent by cyclic voltammetry (details given in Section 2). From the measured redox values (Table 1) it indicates that 4MBT serves as an electron donor in interaction with PCA which in turn behaves as an acceptor. The fourth term in Eq. (1), which represents the Coulomb stabilization parameter has been neglected in computing ΔG^0 as it possesses negligible contribution (~ 0.06 eV) in this highly polar environment. In such highly polar ACN ($\varepsilon_s \sim 37.5$) environment, large values of $-\Delta G^0$ (>2 eV, Table 1) demonstrate the thermodynamic possibility (energetically

Table 1
Redox potential values, values of $E_{0,0}^*$, Gibbs free energies (ΔG^0) for photoinduced ET reactions within the present donor and acceptor molecules in non-polar NH and highly polar ACN solvents at the ambient temperature

Donor	Acceptor	$E_{1/2}^{OX}$ (D/D$^+$) (V)	$E_{1/2}^{RED}$ (A$^-$/A) (V)	$E_{0,0}^*$ (eV)	ΔG^0 (in ACN) (eV)	ΔG^0 (in NH) (eV)
4MBT	PCA	+0.4	−0.9		+1.3	
4MBT[a]	PCA	+0.4	−0.9	4.04	−2.74	−1.24
4MBT	PCA[a]	+0.4	−0.9	3.75	−2.45	−0.95

[a] Denotes the excited singlet state S_1.

favorable) of the occurrence of highly exothermic photoinduced ET reactions [22].

In non-polar medium NH, as it is not possible to measure the redox potentials of the reacting species, an approximate value of ΔG^0 was computed, shown in Table 1, considering the solvation energies in this medium following the procedure adopted by earlier authors [23,24]. From these computed values of ΔG^0, it appears that photoinduced reaction becomes less exothermic in non-polar medium.

3.2. Steady-state electronic absorption spectra of the mixture of the electron donor 4MBT and the acceptor PCA: comparison of these spectra with those observed in the case of the synthesized bichromophores containing the above donor and acceptor systems connected by olefinic, unsaturated and saturated, bridges

The absorption spectra of the donor 4MBT in the presence of the electron acceptor PCA were measured in NH ($\varepsilon_s \sim 2.07$) and highly polar ACN ($\varepsilon_s \sim 37.5$) (Fig. 2) fluid solutions. In both non-polar NH and highly polar ACN media it was found that the spectra of the mixture of 4MBT and PCA are just the superposition of the absorption bands of the individual components. This observation excludes the possibility of formation of any ground state charge transfer (CT) complex within the reactants at room temperature in both the solvents used. Even at large concentrations ($\sim 10^{-2}$ mol dm^{-3}) of the donor and acceptor, the same type of spectral superposition of the individual components were appeared in the absorption spectra of the mixture, irrespective of the polarity of the environments.

On the other hand, the electronic absorption spectra of the bichromophore (4MBA) (Fig. 2) do not show the spectra of the components but instead an overlapping of the two new long wavelength bands of broad nature spanning between 330 and 420 nm in both polar ACN and non-polar NH fluid solutions was found. These bands seem to be due to the two CT bands, one resides at 351 nm and other situated at the 380 nm region. These CT bands are due to the presence of two closely lying higher occupied molecular π-orbitals of benzothiophene and to the lowest vacant *n*-orbital of PCA. The similar observations of the presence of the two CT bands were made earlier [12] in cases of some bichromophoric systems containing derivatives of carbazole as donor part and fluorenone as acceptors and the corresponding oligomers bearing the bichromophores as pendant groups.
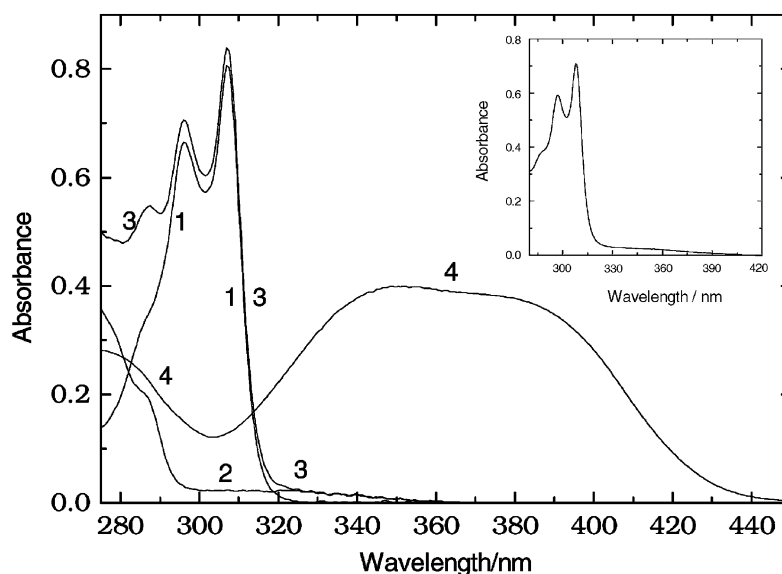

Fig. 2. Steady-state electronic absorption spectra of 4MBT ($C = 5.9 \times 10^{-5}$ mol dm^{-3}, curve 1), PCA ($C = 2.9 \times 10^{-4}$ mol dm^{-3}, curve 2), mixture (curve 3) of 4MBT ($C = 5.9 \times 10^{-5}$ mol dm^{-3}) and PCA ($C = 2.9 \times 10^{-4}$ mol dm^{-3}), Steady-state electronic absorption spectra of 4MBA ($C = 1.8 \times 10^{-5}$ mol dm^{-3}, curve 4) in ACN fluid solution at 296 K. $l = 1$ cm. Inset: steady-state electronic absorption spectra of 4MBAS in ACN fluid solution at 296 K. $l = 1$ cm.

In the case of the other bichromophore 4MBAS, however, both the absorption spectra of the donor and the acceptor part are apparent but additionally a long wavelength (low energy) tail extending down to 410 nm was observed (shown in inset of Fig. 2). This tail seems to originate from the ground state CT interaction between the 4MBT donor and the PCA acceptor.

Thus, significant changes occur in the absorption spectra of the donor 4MBT when it connects with the acceptor PCA by an unsaturated (olefinic) or saturated bridge. As only in case of intramolecular interactions formation of ground state CT complex was apparent, it appears that a particular conformation may exist in the bichromophore through the mutual alignment of the donor and acceptor moieties and it facilitates the formation of the ground state CT.

3.3. Steady-state and time-resolved fluorescence spectra at the ambient temperature

(a) *Intermolecular studies*: It was reported earlier that both in non-polar NH and polar ACN solvents the fluorescence lifetime of 4MBT is about ∼0.17 ns [6]. In the present study, with gradual increase of concentration of the acceptor PCA the intensity of entire fluorescence emission band of 4MBT was found to diminish regularly both in non-polar NH and polar ACN fluid solutions (Fig. 3). PCA itself does not emit fluorescence both at the ambient temperature and at 77 K. Here the concentration of quencher PCA was chosen to be very low (conc.$_{max}$ ∼ 10^{-4} mol dm^{-3}) so that relative to that of the donor 4MBT, its absorbance will be negligible at the excitation wavelength (∼307 nm). In this way possibility of the occurrence of inner filtering effect could be

avoided. As lack of formation of ground state complex was apparent from the absorption spectra of the donor and the acceptor and their mixture, the possibility of the presence of static mode could reasonably be ruled out as one of the possible sources for the observed fluorescence quenching phenomena. Nevertheless, we would consider, as possible sources of quenching, two mechanisms of reactivity: (1) singlet–singlet energy transfer from electronically excited 4MBT to PCA, (2) photoinduced ET. There is a large spectral overlap between the PCA absorption spectrum and the fluorescence emission of 4MBT. We could conclude that energy transfer from the S_1 state of 4MBT to PCA is thermodynamically possible and is a possible quenching pathway in competition with ET quenching process.

In ACN fluid solution, a long wavelength broad band of very weak intensity peaking nearly at 518 nm was found to develop gradually at the expense of the fluorescence emission intensity of 4MBT in the presence of PCA (Fig. 3).

(b) *Intramolecular studies*: When we excite specifically the donor part of the bichromophore (4MBA) using the excitation wavelength 307 nm it was surprisingly observed that the fluorescence band of the 4MBT, spanning between 320 and 350 nm, completely quenched but a long wavelength band of large intensity peaking at about 518 nm, in cases of both 4MBA and 4MBAS, appear (Fig. 3). A band, though very weak in nature, was found at the same energy position, as discussed above, when the donor molecule was found to undergo intermolecular interactions with the electron acceptor PCA. Moreover on direct excitation of the CT absorption band of the bichromophore (4MBA) situated at 351 nm and 4MBAS at 400 nm region a fluorescence band of con-
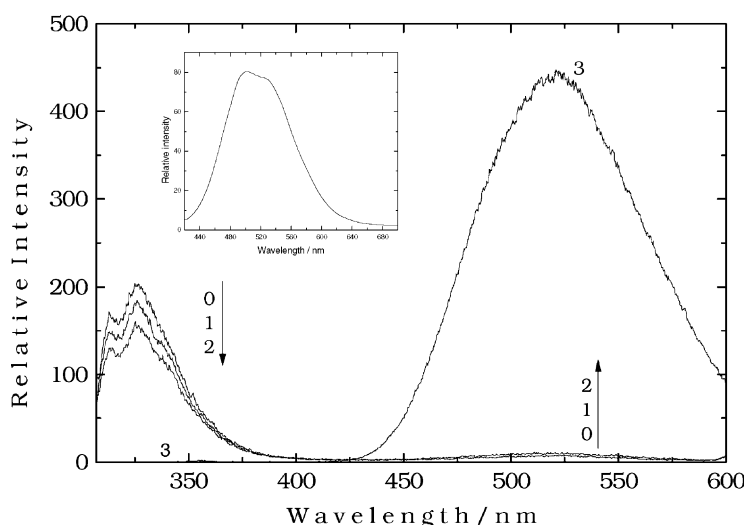

Fig. 3. Fluorescence emission spectra of 4MBT (λ_{ex} = 307 nm) ($C = 2.2 \times 10^{-5}$ mol dm^{-3}) in ACN fluid solution at 296 K in the presence of PCA (curves 0, 1 and 2). Concentration of PCA (mol dm^{-3}) in (0) 0; (1) 1.2×10^{-4}; (2) 5.4×10^{-4}. Curve 3: fluorescence emission spectra of 4MBA ($C = 1.8 \times 10^{-5}$ mol dm^{-3}) in ACN fluid solution at 296 K. Inset: fluorescence emission spectra of 4MBAS ($C \sim 10^{-5}$ mol dm^{-3}) in ACN fluid solution at 296 K.
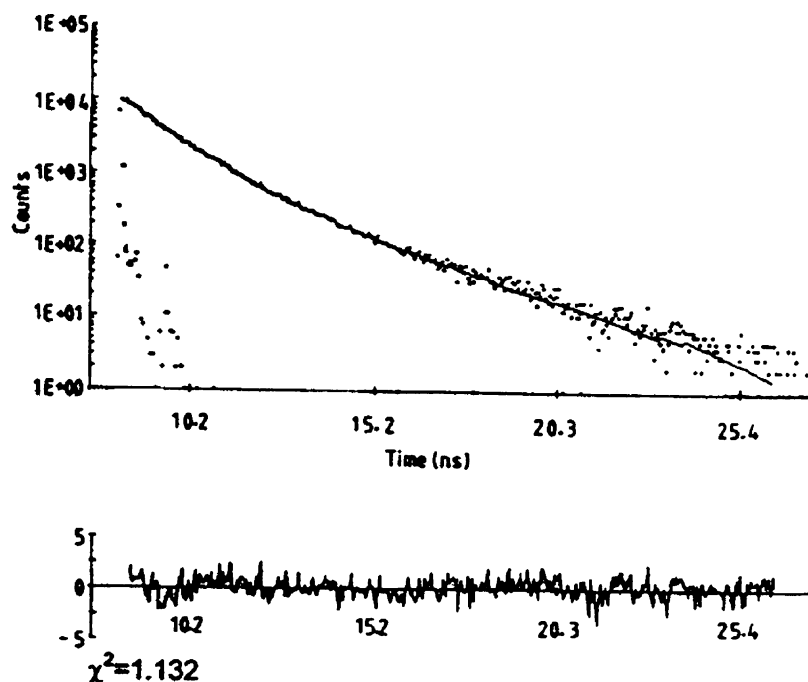
Fig. 4. Fluorescence decay curve associated with lamp profile showing the biexponential decay of 4MBA ($C = 1.8 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$, $\lambda_{em} = 518\,\mathrm{nm}$) in ACN fluid solution at 296 K with corresponding residual.

siderable intensity at the same energy position 518 nm was found.

From the above observations, it shows that 518 nm band should be the CT emission band whose formation is largely facilitated in intramolecular system comprising the donor and the acceptor moieties. Thus it is inferred that both in the ground and excited singlet (S_1) states, a particular conformation through mutual orientation of the donor and acceptor sites is responsible for formation of CT complex.

In non-polar NH solvent, both the bichromophores do not exhibit any fluorescence emission at 296 K. However to elucidate the solvent effect the fluorescence of 4MBA was studied in the different mixtures, containing the different proportions of the two solvents of THF ($\varepsilon_s \sim 7$) and DMF ($\varepsilon_s \sim 36.7$), in which fraction of more polar solvent DMF was gradually increased. As THF does not dissolve in ACN, the mixture of THF/DMF was used. The intensity of fluorescence of 4MBA (nearly same concentration in all mixtures) gradually develops with the increase of the polarity of the resulting mixture of the two solvents accompanied by a continuous red-shift. These observations further corroborate our views that the fluorescence of the bichromophore 4MBA mainly originates from the CT state. The similar trend was observed in the case of the other bichromophore 4MBAS used in the present investigation.

From these observations it was inferred that the architectures of the bichromophoric molecules play an important role in non-radiative depletion mechanism of the excited states of its reacting components. Fig. 4 reproduces the fluorescence decay curve of 4MBA ($\lambda_{em} \sim 518\,\mathrm{nm}$, peak po-

sition) in ACN fluid solution. The biexponential nature of the fluorescence emission of this bichromophore was clearly observed from the decay analysis using Eq. (2). In this equation, light emission has been described as a superposition of two exponential decays

$$I(\lambda, t) = B_1(\lambda) \exp\left(\frac{-t}{\tau_1}\right) + B_2(\lambda) \exp\left(\frac{-t}{\tau_2}\right) \tag{2}$$

where τ_1 and τ_2 are the fluorescence lifetimes associated with the normalized pre-exponential factors B_1 and B_2, respectively.

The fractional contribution (Eq. (3)) $f_i(\lambda_i)$ of each component to the total steady-state intensity is defined as [25,26]

$$f_i(\lambda) = \frac{B_i \tau_i}{\Sigma_j (B_j \tau_j)} \tag{3}$$

and the computed fractional contributions (f_1 and f_2) are found to be 0.7 (for τ_1) and 0.3 (for τ_2), respectively, for the present bichromophoric system.

From these two lifetimes ($\tau_1 \approx 1$ and $\tau_2 \approx 2.6\,\mathrm{ns}$, error $\pm 6\,\mathrm{ps}$) and their fractional contributions (f_1, f_2) it is inferred that there should be two different species involved in fluorescence emission of the bichromophore 4MBA. In high probability, these two species should be due to, the presence of two geometrical isomers, *cis*- and *trans*-forms, of 4MBA. Thus the excited CT band is composed of mainly overlapping of the two emission spectra: one due to *cis* (folded) and the other for *trans*-type (extended) geometry of 4MBA (Fig. 5). It is known that in the ground state *trans*-isomer mainly exists as it is thermodynamically more stable isomer [27].
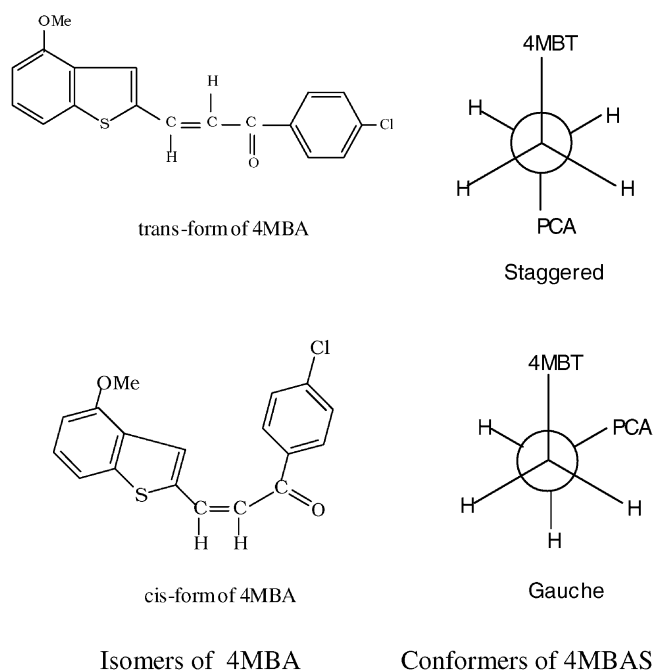
Fig. 5. Molecular structures of possible isomers of 4MBA and possible conformers of 4MBAS.

PCA under alkaline conditions to afford the bichromophoric chalcone in 56% yield, which was characterized from analytical and spectroscopic data. The ^{1}H NMR spectrum of the compound 4MBA revealed the presence of both *cis*- and *trans*-geometrical isomers, with the preponderance of the latter. The coupling constants of the olefinic protons present as characteristic doublets are 5.1 (*cis*-) and 15 (*trans*-) Hz, respectively.

On irradiation of this *trans*-isomer an excited species would be produced which is usually lower in energy than that of the corresponding *cis*-isomer (folded conformation). On monitoring the wavelength at far longer wavelength region, i.e., say at 590 nm of CT fluorescence band, not much change in the lifetime values were noticed but interestingly f_1 (associated with τ_1) reduces to 0.2 and f_2 (fractional contribution of τ_2) becomes 0.8. It is to be noted that excitation spectra corresponding to lower and higher wavelength regions of the emission spectra exactly corresponds to its absorption spectra. This indicates that there is no possibility of impurity emission overlapped with the emission of the molecule studied. Thus the parameters associated with fluorescence lifetimes demonstrate that 2.6 ns species dominates at longer wavelength region and should correspond to *trans* isomer and 1 ns should be responsible due to presence of *cis*-form of 4MBA. An attempt was made to resolve the excited CT band (Fig. 3) by a peak-fit software program (Fig. 6). From the computer-assisted resolution of the band it shows that the fitted curve corresponds very well (Fig. 6) with the experimental spectrum when the latter is resolved into two bands, one being at 515 nm (*cis*-geometry as discussed above) and the other resides at 564 nm region (*trans*-form). It would be relevant to point out here that in intermolecular studies, as

The synthesis of the bichromophore 4MBA was achieved in three steps from 4MBT [6]. The latter was deprotonated in the 2-position with *n*-butyl lithium (THF/−78 °C). Quenching the deprotonated species with *N,N*-dimethylformamide under standard conditions afforded 4MBT-2-carbaldehyde in 62% yield. The compound was characterized from microanalytical and spectroscopic data. The aldehyde reacted with
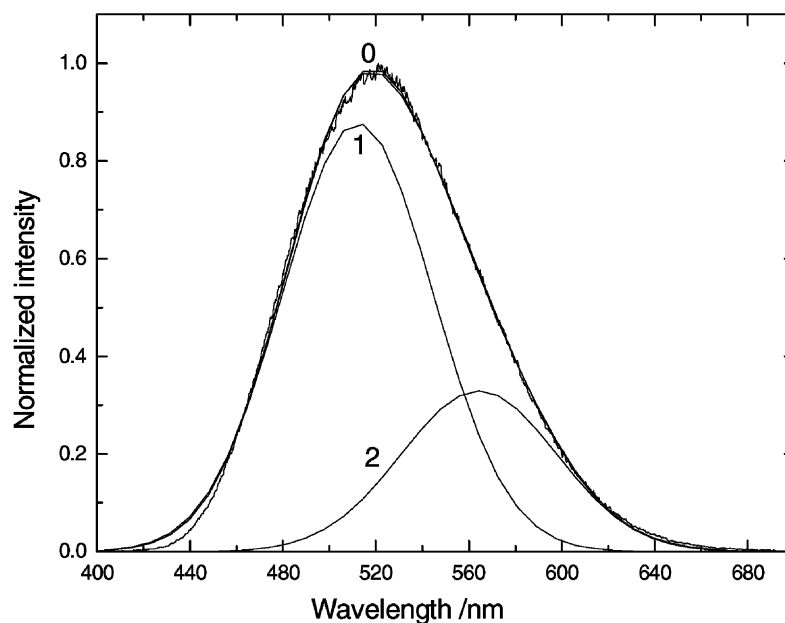

Fig. 6. Computer-assisted (by using peak-fit software) resolution of the steady-state CT fluorescence emission spectra of 4MBA of Fig. 3 (curve 3) into two components (discussion is made in the text). Of the two spectra labeled 0, the solid one is the fitted curve and is the sum of two curves 1 and 2, the other one is the experimental spectrum.

reported above, with gradual addition of PCA, very slow quenching of 4MBT fluorescence was noticed accompanied by the development of a very weak band peaking at around 518 nm region. This long wavelength emission should originate from contact CT complex. However very weak band prevents us from measuring the fluorescence decay of this species but it corroborates our views, made from the different measurements discussed above that the CT fluorescence band of the bichromophore 4MBA, peaking at around 518 nm, should originate from the *cis*-form of the bichromophore 4MBA, because in the folded geometry the donor and the acceptor moieties would be very close to each other to facilitate contact type CT interactions.

In the case of the other bichromophore 4MBAS, measurements of CT fluorescence lifetimes demonstrate the formation of the two different species (biexponential fit was found to be the best one as evidenced from least χ^2 value) having lifetimes 1.7 and 3.5 ns. However since in this bichromophore (Fig. 1) where the donor and the acceptor moieties are connected by a saturated methylene spacer ($-CH_2-CH_2-$), the possibility of formations of different isomers (*cis*- and *trans*-) does not arise. It may therefore be inferred that the two different species are the two different conformations of the bichromophore, viz. "gauche" (reacting partners are close) and "staggered" (partners are far apart) (Fig. 5). Catalytic hydrogenation of **3** in the presence of Pd–C (10%) resulted in the compound **4** in 50% yield. The donor and acceptor moieties in this compound are linked by a saturated spacer. Hydrogenation in the presence of perchloric acid would have reduced the carbonyl function into another $-CH_2-$ group. However this would have reduced the acceptor properties of the moiety, hence we desisted from this. As evident from the spectroscopic studies (see above), existence of this compound in gauche and staggered conformations was discernible.

3.4. Transient absorption measurements

(a) *Intermolecular investigations*. To see experimentally whether photoinduced ET reactions are really occurring within the present D–A systems in ACN solvent, pulsed laser excitation at 355 nm, using Nd:YAG laser system, was used to excite specifically the acceptor PCA moiety used in the present study. This was done to avoid the possibility of occurrences of interfering energy transfer processes, if any, within the present reacting system.

Upon 355 nm laser pulse excitation of the mixture of 4MBT and PCA in ACN fluid solution the transient species at around 370, 440, and 480 nm (Fig. 7) are observed. To assign the 480 nm band metallic sodium (Na) experiment was performed on the steady-state electronic absorption spectra of PCA. One new band near at 480 nm other than that of PCA bands appeared which slowly disappear within 5 min in the presence of molecular oxygen. This shows the band near 480 nm corresponds to
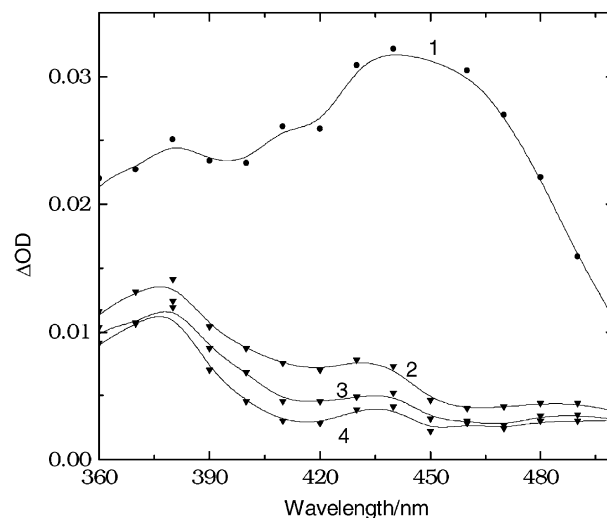

Fig. 7. Transient absorption spectra of PCA (excitation wavelength ~355 nm, laser pulse energy ~150 mJ/pulse) in ACN (conc. ~ 5.6×10^{-2} mol dm^{-3}) at the ambient temperature in the presence of the donor 4MBT (conc. ~ 2.2×10^{-2} mol dm^{-3}) at delay time: (1) 0.5 μs; (2) 3.0 μs; (3) 5.0 μs; (4) 10 μs.

the band of dissociated anions (PCA$^-$) or the anions of the solvent separated species which is formed according to the reaction mechanism below:

$$Na + PCA \rightarrow Na^+ + PCA^-$$
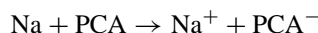
The bands at 370 and 440 nm are due to the cation of benzothiophene as already reported in case of similar benzothiophene molecule [28].

With increase of delay from 0.5 to 3.0 μs significant changes observed in the transient spectra reveal that anions decay at much faster rate than the cationic species.

(b) *Intramolecular investigation*: The transient absorption spectra of the bichromophores 4MBA and 4MBAS have been measured by direct excitation, by using the third harmonic of the Nd:YAG laser system, of the ground state CT complex situates at 355 nm region. A broad transient band peaking at about 480 nm was observed with single lifetime (~2 μs) (Fig. 8). This 480 nm absorption band should be the band of radical anionic species (PCA$^-$), as evidenced from the intermolecular flash photolysis investigations as discussed above. The appearance of a shoulder at around 440 nm indicates the presence of the cationic species of the donor 4MBT. Similar to the observations made in the intermolecular studies, the transient absorption spectra of the bichromophore gradually diminishes with increase of delay times (μs) between the exciting and analyzing pulses. The formation of the excited singlet CT complex $^1(D^+-A^-)$ state was confirmed by its fluorescence (steady-state measurements) but it could not be ascertained in the transient absorption spectra with our present experimental setup due to lack of picosecond delays but from the transient measure-
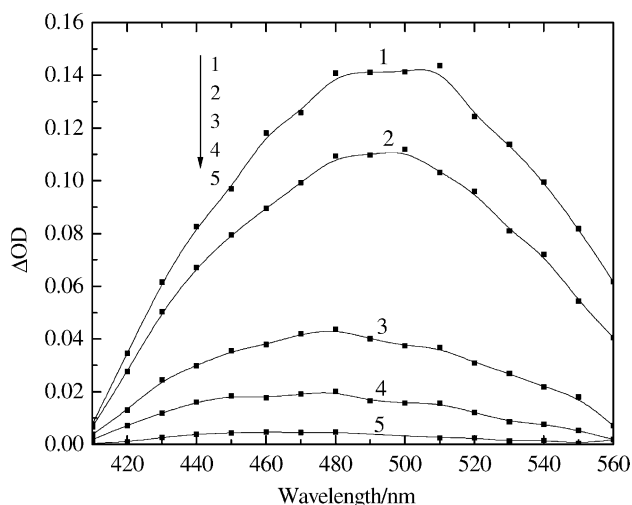
Fig. 8. Transient absorption spectra of 4MBA (excitation wavelength ~355 nm, laser pulse energy ~150 mJ/pulse) in ACN ($C = 1.4 \times 10^{-5}$ mol dm^{-3}) at the ambient temperature at delay time: (1) 0.5 μs; (2) 1.0 μs; (3) 3.0 μs; (4) 5 μs; (5) 10 μs.

ments formation of the long-lived (in μs time domain) triplet $^3(D^+ \cdots A^-)$ state was apparent.

(c) *Estimation of the yield of loose-structured charge separated species (ϕ_R) in case of the bichromophores.* The time profiles of the absorbance of the acceptor PCA anion in ACN at 480 nm observed from intermolecular investigation and absorbance of the bichromophore 4MBA and 4MBAS at the same energy position, which is predominantly due to PCA anion, are reproduced in Figs. 9 and 10.

The decays of the bichromophores in Fig. 10 show the unimolecular first-order decays. This indicates that

480 nm band observed in cases of 4MBA and 4MBAS should be assigned to a mixture of contact ion-pair (CIP) of the acceptor anion. To examine the photoconducting properties of the bichromophores the two rate parameters: rates of ion-pair formation (charge separation rate), k_{CS} (which has been computed from semi-classical approximation of Marcus shown in Eq. (6), vide infra) and charge recombination within contact ion-pair, k_{CR} were estimated. The method of determining the latter rate parameter from the decay of anion and cation is shown below. The knowledge of these two parameters are necessary since the overall photogeneration efficiency depends upon the field induced separation of charge carriers competing with the geminate recombination.

The decay of the absorbance at 480 nm observed in the transient absorption spectra of the bichromophores is represented by a single exponential. Eq. (4) is for the folded conformation where the donor and acceptor moieties would be close to each other and first-order charge recombination process would occur within the ion-pair and formation of loose-structured charge separated species. The ion-pair lifetime (τ_{ip}), defined as in Eqs. (4) and (5) [12].

$$\tau_{ip} = (k_{CR} + k_{CST})^{-1} \tag{4}$$

$$\phi_R = k_{CST}\tau_{ip} \tag{5}$$

k_{CR} and k_{CST} denote the charge recombination and loose-structured charge separated (equivalent to charge dissociation in intermolecular cases) rates, respectively. In intramolecular ET process, i.e., for the case of the bichromophores no ionic dissociation is possible but loose structures of them could be formed in highly polar solvent ACN where there will be no contact between the donor
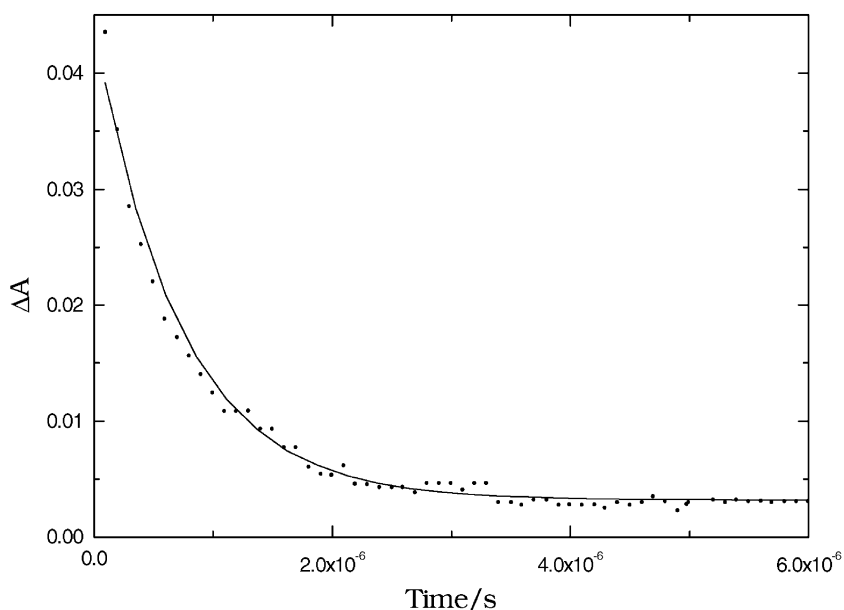

Fig. 9. The time profile of the absorbance (ΔA) of the anion radical of the acceptor PCA in the presence of 4MBT at 480 nm.
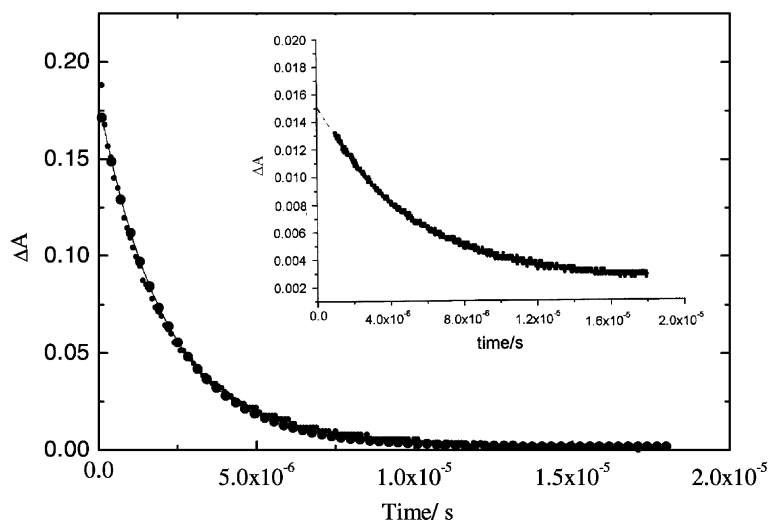
Fig. 10. The time profile of the absorbance (ΔA) of the bichromophore (4MBA) at 480 nm. Inset: the time profile of the absorbance (ΔA) of the bichromophore (4MBAS) at 480 nm.

and acceptor moieties. Following Verhoeven [29–32] we could define the loose structure as charge separated state (CST) and the corresponding rate has been named as k_{CST} in case of the bichromophores. In bichromophores where photoinduced ET occurs intramolecularly, ϕ_R is the yield of the loose-structured charge separated species. This ϕ_R is defined as the ratio of the concentration of loose-structured charge separated species, formed at the long delay time ($\geq 10\,\mu s$) to the concentrations of the contact ion-pair complex formed initially ($t = 0$) by forward ET reactions. This parameter is equivalent to the yield of the dissociated ion radical or solvent separated ion pair (SSIP) formation in intermolecular systems defined as before. In intramolecular system ϕ_R is evaluated experimentally [12] by taking the ratio of the absorbance due to loose-structured charge-separated species formed at the long delay time used and the initial value estimated by extrapolating the ion-absorbance to $t = 0$ in Fig. 10.

The τ_{ip}, ϕ_R, k_{CR} and k_{CST} values obtained from the transient absorption decay of the bichromophores 4MBA and 4MBAS are shown in Table 2. All the above parameters were also measured from the cationic decay (using 440 nm wavelength of the transient absorption spectra). As contribution of k_{CST} is very small relative to k_{CR}, the observed τ_{ip} shows approximately the charge recombination within the ion-pair complex.

In bichromophoric systems 4MBA and 4MBAS, k_{CR} values computed from the cationic decays are found to be similar to those obtained from the analysis on the decay of anionic species (Table 2).

The rate of formation of ion-pair (forward ET or charge separation rate), k_{CS}, which occurs at the early stage of the delays used in the measurement of transient absorption spectra was determined by using the

Marcus semiclassical treatment approximation [12] as shown below:

$$k_{cs} = \left(\frac{\pi}{\hbar^2 \lambda_s(R) k_B T} \right)^{1/2} |V(R)|^2 \sum_{j=0}^{\infty} \left(\frac{e^{-s} S^j}{j!} \right)$$

$$\times \exp \left[- \left\{ \frac{(\Delta G^0 + \lambda_s(R) + jh\upsilon)^2}{4\lambda_s(R) k_B T} \right\} \right] \qquad (6)$$

The meaning of the symbols have been described elsewhere [12].

To make sure in using Eq. (6) in the present situation the non-adiabaticity of the ET process has been tested by Eq. (7)

$$A = 4\pi |V(R)|^2 \frac{e^{-s} \tau_1}{\lambda_s(R) \hbar} \qquad (7)$$

As the value of A was found to be $\ll 1$, the ET reactions within the present systems should proceed through non-adiabatic process and Eq. (6) could be safely used in computing k_{CS}.

Table 2
The values of the charge separation rates (k_{CS}) (computed from Eq. (6)), rates of charge recombination (k_{CR}) and formation of loose-structured charge-separated species (k_{CST}) in ACN for the bichromophores 4MBA and 4MBAS, values of yield, ϕ_R, of loose-structured charge-separated species (the measurements were made at the ambient temperature) and τ_{ip} (approximately equal to the charge recombination lifetime within the ion-pair complex)

System	k_{CS} (s^{-1})	ϕ_R[a]	k_{CR} (s^{-1})	k_{CST} (s^{-1})	τ_{ip} (μs) (± 0.01)
4MBA	7.7×10^8	0.01	5.0×10^5	4.8×10^3	2.11
4MBAS	7.7×10^8	0.16	2.0×10^5	3.0×10^4	4.81

[a] In intramolecular system as no ionic dissociation is possible this yield should correspond to loose-structured charge separated species (CST).
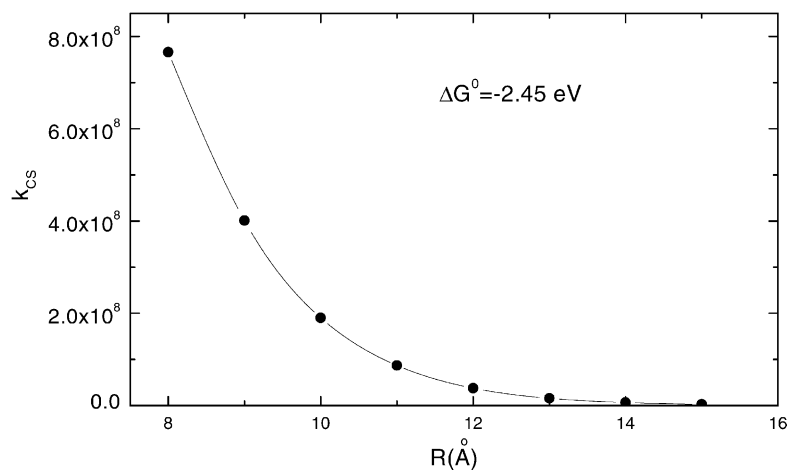
Fig. 11. Dependence of first-order ET rate constant (k_{CS}) on the distance of separation (R) for the D–A pairs in ACN fluid solution at 296 K ($\Delta G^0 \sim -2.45$ eV).

In case of the bichromophores the k_{CS} values were computed assuming R (distance of separation between the donor and the acceptor moieties) be equal to the contact distance between the donor and acceptor. In support of this proposition it could be stated that k_{CS} values, computed at the different magnitudes of R, decrease significantly as R increases beyond the contact distance (Fig. 11). As the above experimental findings demonstrate that in bichromophore 4MBA *cis*-form is dominating over *trans*- one and in 4MBAS more flexible spacer has been used the value of R should logically be assumed to be very close to the contact distance.

The values of k_{CS} and k_{CR} for the intramolecular (in the cases of the bichromophores 4MBA and 4MBAS) ET processes are shown in Table 2. The values of the rates of charge recombination process (back ET) within the contact ion-pair complex, k_{CR}, which are obeying the first-order kinetics, in case of the two bichromophores (4MBA and 4MBAS) are the order of 10^5 s^{-1} (Table 2). Similar slow recombination rates within contact ion-pair complex are also observed by Fukuzumi et al. [33] for back ET of first-order kinetics in case of many other bichromophoric or multichromophoric systems. From the table it is apparent that when nature of the spacer in the bichromophores is changed from unsaturated (in case of 4MBA) to more flexible saturated (in 4MBAS) one by which the redox centers are connected together, the rate of energy wasting process, k_{CR} decreases considerably relative to k_{CS} and consequently ϕ_R increases. It seems mutual conformations of the chromophoric units in the bichromophores have great influence on the formation of charge separated species and consequently the energy wasting back ET (charge recombination) process is largely impeded specially in the case of 4MBAS where the donor and the acceptor moieties are connected by a flexible saturated spacer.

The decay shown in Fig. 9, observed from the case of the intermolecular interactions, does not correspond to the true first-order decay (first-order fitting looks bad from correlation coefficient value). Possibly charge recombination occurs not only within contact ion-pair but also fully dissociated cations and anions formed in highly polar ACN due to intermolecular interactions recombine slowly, by second-order diffusion process, after charge dissociation. The decay becomes complicated. However, as the knowledge of the rate parameters k_{CS} and k_{CR} is very much important in testing the photoconducting properties of the bichromophores we were interested in the decay analysis of the Fig. 10 only which corresponds to these intramolecular systems.

4. Concluding remarks

From the above results derived from both steady-state and time-resolved spectroscopic measurements it reveals that mutual orientation between the donor and the acceptor moieties in a linked system exhibits significant role in facilitating the CT complex both in the ground and electronic excited states. In intermolecular interactions the formation of excited singlet (S$_1$) CT complex of contact nature has been suggested. However in intramolecular cases, two distinct excited state isomers/conformers were apparent from the steady-state and time dependence behaviors of the complexes. Laser flash photolysis measurements indicate that energy wasting charge recombination process could be largely prevented in a bichromophoric system when its constituent redox sites are connected by a flexible methylene spacer rather than an unsaturated linkage. Possibly the energy wasting process (CR) could be further minimized if a little restriction in the flexibility of the spacer be imposed. This could be done by incorporating the two spacers instead of one (cyclophane type) between the donor and the acceptor

sites so that a particular configuration where the donor and the acceptor moieties would be very close (<3 Å), one over the other, and in a position of face to face orientation would be predominant. Synthesis of such bichromophoric systems and their photophysical investigations are in progress in our laboratory.

Acknowledgements

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