Investigation of excited state electron-transfer reactions. A search for other associative processes

R. DE, S. BHATTACHARYYA* and T. GANGULY[†]

Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700032, India

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Abstract—The present investigations were carried out to reveal the nature of the photoinduced electrontransfer (ET) process within the electron donors 1,2,3,4-tetrahydroquinoline (THQ) and 1-methyl-1,2,3,4tetrahydroquinoline (THMe), and widely used acceptor tetracyanoquinodimethane (TCNQ) in the highly polar solvent acetonitrile (ACN) at 300 K. Observations of considerable overlapping between the emission spectrum of the donor molecules studied in the present investigation and the electronic absorption spectrum of the acceptor TCNQ, coupled to a high negative value of ΔG [the energy gap between the locally excited (LE) and radical ion pair (RIP) states] when one of the chromophores is excited, indicate the possibility of concurrent occurrence of the two processes, e.g. energy and electron transfer. Surprisingly even when the donor chromophore is photoexcited, no spectral manifestation of energy transfer was observed, though both steady state and time resolved (in the time domain of nanosecond order) spectroscopic measurements strongly suggest the occurrence of a highly exothermic ET reaction within the present donor-acceptor systems. Furthermore such ET reactions have been suggested to occur between donor and acceptor separated by a large distance (~7 Å), and quenching of fluorescence emission of donor molecules is caused primarily due to outer sphere ET reactions with the acceptor. Measured electron transfer rates $(k_{\rm ET})$ were found to be of much lower value ($\sim 10^7 \, \text{s}^{-1}$). It is demonstrated that loose structure of the transient geminate ion pair complex is formed due to the encounter between excited acceptor (or donor) and unexcited donor (or acceptor), and due to this structural property, a stable anionic species (TCNQ⁻ ion) is produced due to the rapid dissociation (probably in the picosecond time domain) of this excited complex. It is hinted that synthesis of biochromophoric systems in which the present donor and acceptor chromophore would be linked by a polymethylene type (σ -type) spacer might be useful in building good photoconducting materials.

INTRODUCTION

PHOTOINDUCED electron transfer (ET) reaction in different electron donor and acceptor systems has received increasing interest for elucidating the functions of the organized chromophores in the photosynthetic reaction centres [1]. During the last few decades both experiments and theory of electron transfer have made significant progress [2–16]. Highly efficient exothermic ET reactions, mimicking photosynthesis, were observed in the cases of several bichromophoric systems of electron donors and acceptors linked together by a spacer of the polymethylene type, and the corresponding oligomer systems where these bichromophores are present as pendant groups [16]. These systems exhibit highly efficient photoconducing properties [16] and hence synthesis of these organic-based photoconducting materials has tremendous commercial importance, especially in the electrophotographic/xerographic, duplicator industries. Also these materials could be used to build molecular electronic devices [17, 18].

The highly exothermic ET reactions generally occur in the "Marcus inverted region" where a slower reaction rate, due to restriction of the Franck-Condon factor, with increasing exothermicity is observed [19]. Thus, in the studies of such types of ET reactions, testing of the Marcus theory has nowadays become a useful practice [16, 20, 21]. Several attempts have been made previously to find the inverted region experimentally. REHM and WELLER [22] proposed a correlation between the fluorescence quenching rate constant k_q and the free energy change ΔG for photoinduced ET reactions in the cases of some typical electron donor-acceptor systems in acetonitrile solvent. The correlation was in good agreement with the Marcus electron transfer theory [but in the normal region (endothermic or slightly exothermic ET reaction)] and no

^{*} Present address: Chemistry Department, Bijoygarh J. R. College, Calcutta-700032, India.

[†] Author to whom correspondence should be addressed.

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inverted region was observed as predicted by Marcus theory in the highly exergonic region; instead, a diffusion-limited rate was found there. Later on, MILLER *et al.* [2] demonstrated a rapid increase of the ET rate in the mildly exergonic region and a considerable decrease of ET rate in the highly exergonic region in the case of intramolecular ET between a donor and acceptor which are linked by a spacer. In the case of the intermolecular ET reaction MATAGA *et al.* [23] demonstrated the energy gap dependence of the charge recombination (CR) reaction of the ion pairs produced by photoinduced electron transfer in the inverted region which was proposed by MARCUS [24, 25].

The aim of our research group is to develop different organic-based bichromophoric systems of electron donor and acceptor linked by single and double spacers of polymethylene type (σ -spacer). These bichromophoric systems are expected to serve as efficient organic photoconducting materials which might be used in the photocopier, duplicator and microcircuitry industries. Hence, prior to the synthesis of such types of materials, our main purposes are: (1) to choose different electron donor and acceptor molecules where highly exothermic electron transfer (ET) reactions could occur; and (2) to study systematically the intermolecular ET reaction along with associative processes, since the studies on intermolecular interaction would be helpful to us to reveal the nature of the intramolecular ET mechanism if these donors and acceptors could be linked through polymethylene type spacers which were used by several authors [16] to develop efficient photoconducting materials.

In the present investigations tetracyanoquinodimethane (TCNQ) has been chosen as the electron acceptor (A) molecule. TCNQ has been widely used, by earlier workers, as a strong electron acceptor [26–30] to form highly conducting CT complexes. Presently, we are interested in searching for potential electron donors capable of undergoing efficient ET reactions with TCNQ. In the present paper we will disucss our results considering the two following electron donors: (a) 1,2,3,4-tetrahydroquinoline (THQ); and (b) 1-methyl-1,2,3,4-tetrahydroquinoline (THMe). In this work, with these donors and the acceptor TCNQ, studies were mainly made by both steady state and time resolved (in the time domain of nanosecond order) spectroscopic methods to reveal the nature of intermolecular ET reactions in acetonitrile (ACN) fluid solution at 300 K. In the framework of Rehm–Weller and Marcus theory and from observations of spectral overlap between donor emission and acceptor absorption, an attempt was made to observe the role of the other important associative process, energy transfer (if it exists), along with the electron transfer process. In this communication the results are described.

EXPERIMENTAL

Materials

The sample 1,2,3,4-tetrahydroquinoline (THQ) supplied by Fluka, Switzerland was used after distillation under reduced pressure. Another sample 1-methyl-1,2,3,4-tetrahydroquinoline (THMe) was synthesized, the details of which are given below. Tetracyanoquinodimethane (TCNQ) and hydroquinone (HQ) obtained from Aldrich were purified by repeated recrystallization in acetonitrile (ACN) solvent. The solvent ACN (E. Merck) of spectroscopic grade was distilled under vacuum and tested for absence of any emission in the wavelength regions studied. Tetrahydrofuran (THF) of spectroscopic grade obtained from BDH was refluxed with LiAlH₄ for 2 h followed by distillation.

Apparatus

The electronic absorption and emission spectra were recorded with the help of a Shimadzu UV-vis spectrophotometer model 210A and a Perkin-Elmer model MPF 44A fluorescence spectrophotometer, respectively. Fluorescence lifetimes of samples were measured by using a time-correlated, single photon counting fluorimeter (model 199, Edinburgh Instruments, U.K.) with a conventional L-format arrangement. All solutions were deoxygenated by purging a N₂ gas stream for 30 min. Electrochemical measurements were done by using the PAR model 370-4 electrochemistry system.



Fig. 1. (a) Electronic absorption spectra of TCNQ in ACN fluid solution $(8 \times 10^{-6} \text{ mol dm}^{-3})$ at 300 K. Concentration of THQ (mol dm⁻³) in (0) 0; (1) 4×10^{-4} ; (2) 8×10^{-4} ; (3) 1.2×10^{-3} ; (4) 1.6×10^{-3} ; and (5) 2.4×10^{-3} . (b) Electronic absorption spectra of TCNQ in ACN fluid solution $(1.0 \times 10^{-5} \text{ mol dm}^{-3})$ at 300 K. Concentration of THMe (mol dm⁻³) in (0) 0; (1) 4×10^{-4} ; (2) 8×10^{-4} ; (3) 1.2×10^{-3} ; (4) 1.6×10^{-3} ; and (5) 2.0×10^{-3} .

Synthesis and characterization

Preparation of 1-methyl-1,2,3,4-tetrahydroquinoline (THMe). To a stirred solution of 1,2,3,4-tetrahydroquinoline (4 g, 300 mmol) in 70 ml of acetonitrile was added 16 ml (200 mmol) of 37% aqueous formaldehyde at 25° in one portion. Sodium cyanoborohydride (2.72 g, 43.5 mmol) was then added to this mixture under nitrogen atmosphere in portions over a few minutes. A vigorous exothermic reaction ensued and a dark coloured residue separated. The reaction mixture was stirred for 30 min and then glacial acetic acid was added dropwise until the solution tested neutral on pH paper. Stirring was continued for an additional 45 min and glacial acetic acid was added frequently to maintain the pH neutrality. The solvent was evaporated under reduced pressure and 50 ml of 2(N) KOH was added to the residue. The resulting mixture was extracted with three 50 ml portions of ether. The combined organic extracts were washed with saturated NaCl solution, dried over anhydrous K_2CO_3 and concentrated. The resulting dark oil was distilled *in vacuo* to give 3 g (68%) 1-methyl-1,2,3,4-tetrahydroquinoline as a colourless oil, b.p. 70–73°/0.4 Torr [31].

¹H NMR (CCl₄): $\delta = 7.06-6.3$ (m, 4H, Ar–H), 3.1 (t, 2H, J = 7 Hz, $-N-CH_2$), 2.76 (S, 3H, $-N-CH_3$), 2.66 (t, 2H, J = 6 Hz, Ar–CH₂), 2.1–1.63 (m, 2H, $-CH_2$).

RESULTS AND DISCUSSION

Electronic absorption and charge transfer (CT) spectra in the ground state at 300 K

Figure 1(a) and (b) shows that the intensity of the ${}^{1}L_{b}$ absorption band system of the electron acceptor TCNQ at 300 K in dilute solution of ACN gradually decreases with the concomitant development of two long wavelength broad absorption band systems around the 420 and 438 nm regions with the increase of concentration of electron donor THQ [Fig. 1(a)] or THMe [Fig. 1(b)]. It was reported in our previous communication [32] that the long wavelength band situated at 420 nm might be assigned as the absorption band of TCNQ⁻ ions [32, 33]. The first absorption band system at about the 438 nm region could be ascribed to a ground state CT band [Fig. 1(a) and (b)] resulting from the interaction between electron donor and acceptor studied in the present investigations. In ACN which is known as an ionizing solvent, several instances of simultaneous occurrence of CT and radical ion absorption bands were reported earlier by some authors [34, 35]. The presence of an isobestic point at about the 427 nm region [Fig. 1(a) and (b)] indicates that the formation of the ground state CT complex is in equilibrium with the component species donor and acceptor. It was reported earlier by

MELBY et al. [33] that different π -complexes of TCNQ molecules with suitable electron donors may dissociate in ACN solution into the corresponding ion-radical. From Fig. 1(a) and (b) the simultaneous appearance of both CT band (~438 nm) and TCNQ⁻ ion absorption band (420 nm) corroborates their propositions also in the case of the present donor-acceptor systems. It appears that with the formation of a CT absorption band at about the 438 nm region, anionic radical ion species of the TCNQ (TCNQ⁻ ion) is formed concomitantly due to the dissociation of this CT complex in ACN solution and this ion absorbs at nearly the 420 nm region. The TCNQ⁻ ion absorbance at the same energetic position was reported earlier by MELBY et al. [33]. It was reported by JONES and MOULI [36] that the radical anion of quinone (Q⁻) absorbs at about the 425 nm region. However, the absorbing wavelength of cationic species is not known. It is expected that the cation is also formed simultaneously.

The same trend of lowering, as observed above, in the ${}^{1}L_{b}$ electronic absorption band of electron donors THQ or THMe (λ_{max} at about the 306 nm region) in dilute solution of ACN is observed with the gradual addition of electron acceptor TCNQ. Moreover with this lowering of donor absorption intensity the simultaneous development of two long wavelength absorption band systems was found to occur at the same energetic positions as observed when the situation was reversed, i.e. when studies were made on the changes of electronic absorption spectra of the acceptor TCNQ due to addition of donor molecules.

The above studies confirm the formation of the ground state CT complex between electron donor THQ or THMe and electron acceptor TCNQ in ACN dilute solution at 300 K and the dissociated $TCNQ^-$ ion from this CT band in this highly polar or ionizing solvent ACN.

Steady state fluorescence emission spectra of electron donors THQ and THMe at 300 K and their changes in the presence of the electron acceptor TCNQ

At 300 K in ACN fluid solution structureless fluorescence emission bands of both THQ $(\lambda_{max} \sim 344 \text{ nm})$ and THMe $(\lambda_{max} \sim 352 \text{ nm})$ are observed [Fig. 2(a) and (b)] when excitation was made in their respective (0, 0) ${}^{1}L_{b}$ absorption band regions. With the gradual addition of acceptor TCNQ in the binary solution of donor THQ (or THMe) in ACN, a regular decrease of donor fluorescence intensity is observed [Figs 2(a) and (b)]. It should be mentioned here that in the changes of donor fluorescence spectra due to the addition of acceptor TCNQ in the mixture of donor and ACN solvent (keeping the concentration of donor molecules fixed) only the hypochromic effect is observed, i.e. no significant change in spectral position of donor fluorescence due to addition of acceptor TCNQ a weak fluorescence band around the 432 nm region is developed [Fig. 2(c)].

It is well known that basic emission quenching reactions are energy transfer and electron transfer processes. In some cases both processes were observed to occur concurrently, expecially in fluid solutions [37-40]. Competition between energy and electron transfer (ET) processes had been reviewed by WILKINSON [37] and KAVARNOS and TURRO [41]. In bimolecular quenching reactions fluorescence quenching might occur, apart from energy transfer or electron transfer processes, through: (1) the formation of ground state complexes (inner filter effect); and (2) excited state intermolecular interactions such as excited state H-bonding. As the changes in the fluorescence emission of donor molecules THQ or THMe [Fig. 2(a) or (b)] occur at much lower concentration ($\sim 10^{-5}$ mol dm⁻³) of electron acceptor TCNQ than those used for absorption measurements to make significant changes in the donor absorption (where concentration of acceptor TCNQ was $\sim 10^{-2}$ mol dm⁻³) the process (1) could be ignored. The possibility of excited state intermolecular H-bonding interactions [process (2)] might be ruled out from the observation of the same trend of lowering in fluorescence emission intensity of both THQ and THMe (where the H of the NH group is replaced by CH₃) in the presence of electron acceptor TCNQ. Thus the remaining routes through which the

nonradiative deactivation of the singlet S_1 state of the donor molecule might occur are energy transfer and photoinduced electron transfer processes. In the case of excitation of the donor both the above processes might be operative since electronic energy levels (S_1 or T_1) of the donors, studied in the present investigations, lie higher than those of the acceptor TCNQ. However, TCNQ has been known as a strong electron acceptor [26– 30, 33] for a long time. Hence, it is quite logical to presume that ET processes between the donor THQ (or THMe) and TCNQ must have a significant role in the lowering of the fluorescence emission of donor molecules, but the occurrence of $S_1^D \rightarrow S_1^A$ energy transfer as an associative process could not be ignored due to the presence of considerable overlap between the emission spectrum of the donor molecule and the electronic absorption spectrum of the acceptor.

Thus from the consideration of good spectral overlapping between the donor fluorescence emission and the acceptor electronic absorption spectrum we have calculated the value of R_o , the critical transfer distance, by using the Förster mechanism of energy transfer (long range dipole-dipole interaction) [42-44] which was found to be 70 Å in the case of donor THQ (or THMe) and acceptor TCNQ systems.



Fig. 2. (a) Fluorescence emission spectra of THQ in ACN fluid solution (3.2×10⁻⁴ mol dm⁻³) at 300 K (λ_{exc} 306 nm). Concentration of TCNQ (mol dm⁻³) in (0) 0; (1) 9.6×10⁻⁶; (2) 1.92×10⁻⁵; (3) 2.88×10⁻⁵; and (4) 3.84×10⁻⁵. (b) Fluorescence emission spectra of THMe in ACN fluid solution (1.4×10⁻⁴ mol dm⁻³) at 300 K (λ_{exc} ~ 307 nm). Concentration of TCNQ (mol dm⁻³) in (0) 0; (1) 5×10⁻⁶; (2) 9.6×10⁻⁶; (3) 1.92×10⁻⁵; and (4) 2.88×10⁻⁵; and (5) 3.84×10⁻⁵. (c) The solid curve exhibits the presence of long wavelength emission band (432 nm) of THQ in presence of acceptor TCNQ in highly polar and ionizing solvent ACN. The dashed curve shows the disappearance of this long wavelength (432 nm) band in THF solvent.

It has been discussed above that due to the excitation of the donor chromophore in the mixture of donor and acceptor TCNQ, the lowering of donor fluorescence emission was accompanied by the development of a weak band at about the 432 nm region [Fig. 2(c)]. We have tested the solvent polarity effect on this long wavelength fluorescence emission band at about the 432 nm region. Interestingly it is observed that the band disappears when the solvent, in which the present donor and acceptor interact, is changed from ACN ($\varepsilon_0 \sim 37.5$) to THF ($\varepsilon_0 \sim 7.58$), a solvent of lower dielectric constant. If the band originates from the $S_1^D \rightarrow S_1^A$ energy transfer process one should expect the presence of the band irrespective of solvent polarity. Further, this observation also indicates that such a band cannot be assigned as an excited CT band since its emission intensity decreases with decrease of polarity of the solvent (from ACN to THF). Thus logically one might propose that this fluorescence emission results from the stable anionic (TCNQ⁻ ion) state, the formation of which may be facilitated in highly polar or ionizing solvent ACN. It has been discussed above in the section "Electronic absorption and CT spectra" that the electronic absorption spectra of anionic species have been observed in the cases of the present donor and acceptor systems. As this radical ion should originate from the dissociation of the geminate ion pair or contact ion pair (CIP) complex it seems very short lived (transient), and the loose structured geminate ion pair is responsible for the production of the stable $TCNQ^{-}$ ion which emits at about the 432 nm region. In favour of the argument that this emission corresponds to TCNQ⁻ ion emission it should be mentioned that a weak emission band at about the same energetic position $(\sim 432 \text{ nm})$ is observed when 420 nm of the electronic absorption spectra of TCNQ (which was assigned as the absorption of radical ion TCNQ⁻) is excited.

However it is well known that excitation of the acceptor moiety is the only possible way to avoid energy transfer and to maintain a reasonable electron transfer (ET) possibility in these donor-acceptor systems. In the following section changes in the acceptor fluorescence emission due to addition of donor molecules in ACN fluid solution have been discussed.

Steady state fluorescence emission spectra of electron acceptor TCNQ in ACN fluid solution at 300 K in the presence of electron donor THQ or THMe in the ground state

Figure 3 shows that when donor THQ (or THMe) is added gradually to the TCNQ-ACN binary solution (keeping TCNQ concentration fixed), the intensity of the fluorescence emission spectrum ($\lambda_{max} \sim 430 \text{ nm}$, Fig. 3) of the acceptor TCNQ is enhanced significantly accompanied by a small red shift $(2 \text{ nm or } 108 \text{ cm}^{-1})$. This observation is somewhat unusual if the S_1 state of the acceptor TCNQ is involved in ET reaction with the donor molecules. In that event one should expect efficient quenching of acceptor fluorescence. The most plausible cause for this phenomenon, which was also discussed in our previous communication [32], might be due to the dissociation of the geminate ion-pair (formed owing to the exothermic ET reaction when the acceptor is excited); the TCNQ⁻ ion, which is observed to emit at the 432 nm region (as discussed above), is produced in ACN solution. The discussions about the dissociation of the ground state CT complex into the TCNQ⁻ ion in ACN fluid solution have been made in the section on "Electronic absorption and CT spectra". It is possible that when TCNQ is excited directly in the presence of the electron donor the formation of the excited charged species of the TCNQ⁻ ion, resulting from ET reaction, is favoured which emits at about the 432 nm region (Fig. 3). With the gradual increase of donor concentration (Fig. 3) the transient geminate ion-pair complex formed by ET reaction between the excited (S_1) acceptor TCNQ and ground state donor may produce more TCNQ⁻ ions due to its rapid dissociation in ACN solution. This might be the case for the observed enhancement of the fluorescence spectra of TCNQ⁻ upon addition of electron donor molecules (Fig. 3). Thus one would expect that when ET reactions occur between excited donor and ground acceptor, the anionic emission band should also be observed at the same (\sim 432 nm) energetic position. This is actually what we noticed (the discussion of which has been given above) when we excited the donor molecule in the presence of the



Fig. 3. Fluorescence emission spectra of TCNQ in ACN fluid solution $(8 \times 10^{-6} \text{ mol dm}^{-3})$ at 300 K ($\lambda_{exc} \sim 390 \text{ nm}$). Concentration of THMe (mol dm⁻³) in (0) 0; (1) 4×10^{-4} ; (2) 8×10^{-4} ; (3) 1.2×10^{-3} .

acceptor TCNQ [Fig. 2(c)]. Thus it might be concluded from the observations of excitations of either donor or acceptor moieties that ET reactions have a significant role even when the donor is excited. On the other hand, we did not find any evidence for occurrence of energy transfer between THQ (or THMe) and TCNQ systems even when the donor is excited. This is quite surprising because large spectral overlap between donor emission and acceptor electronic absorption indicates high probabilities of $S_1^D \rightarrow S_1^A$ energy transfer, especially when the donors possess higher-lying energetic levels than those of the acceptor TCNQ.

Further search for possibilities of energy and electron transfer processes within the present donor-acceptor systems at 300 K

(a) Electron transfer possibility in the D-A system. The possibility of the electron transfer process could be measured in terms of the free-energy change ΔG of the electron transfer step.

From the well-known REHM-WELLER relationship [45, 22] the free energy change ΔG associated with radical ion-pair formation could be evaluated [16] from

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

where $E_{1/2}^{OX}(D/D^+)$ and $E_{1/2}^{RED}(A^-/A)$ are the half-wave oxidation potential of the donor and half-wave reduction potential of the acceptor, respectively. These two parameters have been measured by electrochemical measurements, the details of which have been given in the Experimental section. $E_{0,0}^*$ is the lowest excited electronic state where the ET reaction occurs. The fourth term is the Coulomb stabilization term which measures the gain in free energy in bringing the two ions to the encounter distance R. It was reported earlier [38] that when the solvent has a large dielectric constant value e.g. ACN ($\varepsilon_s \sim 37.5$) the Coulomb energy term might be neglected. Neglecting the fourth term in Eqn (1) we have calculated the value of ΔG for the present donor-acceptor systems. The values of ΔG , for the present donor-acceptor systems, due to excited singlet donor or excited singlet acceptor and also for the ground state donor and acceptor, are shown in Table 1. The large negative values of ΔG ($\Delta G < 0$) (Table 1), when one of the chromophores (donor or acceptor) is in the electronic excited state, clearly demonstrates that ET from the donor chromophore to the acceptor chromophore is exergonic and energetically probable [46, 47]. Especially when the donor is excited, the large negative value of ΔG ($\Delta G \sim -3.10 \text{ eV}$, Table 1) indicates the possibility of occurrence of highly exothermic ET reactions. Following KIKUCHI [48] one might suspect that in this highly exothermic region [ΔG , the energy gap between locally excited (LE) state and radical ion-pair (RIP) state, $\sim -3.10 \text{ eV}$] the quenching in ACN solvent due to ET reactions occurs at a long distance (≥ 7 Å) between donor and acceptor, yielding radical pairs. It might be proposed, following KIKUCHI [48], that in the present systems of donor and acceptor, quenching observed in fluorescence emission of donor is caused primarily due to outer-sphere ET, i.e. full ET reactions. Further, Kikuchi reported that when R (centre-to-centre distance between fluorescer donor and quencher acceptor) \gg 3 Å, the exciplex or geminate ion-pair becomes the secondary quenching product since only the outer-sphere ET can induce quenching at such a long distance. In the present investigations of ET, this mechanism seems to be operative as the value of R has been logically assumed to be ca 7Å from the large negative value of ΔG (-3.10 eV) [48]. In some cases earlier authors [23, 49] used the same value of $R (\sim 7 \text{ Å})$ to study ET reactions in dilute solutions.

(b) Energy transfer possibility in D-A system. It has been mentioned above that the value of R_0 [the critical transfer distance (for long-range dipole-dipole interactions)], has been calculated from the consideration of spectral overlap of donor emission and acceptor electronic absorption, and was found to be ~70 Å in the cases of both THQ-TCNQ and THMe-TCNQ systems. As the value of R has been proposed to be ca 7 Å, the theoretical efficiency of the Förster-type energy transfer calculated from the relation

$$T = \frac{(R_0/R)^6}{1 + (R_0/R)^6},$$
(2)

is found to be nearly 99.99%. It could be presumed, from the observed large value of R_0 , that the Dexter mechanism will obviously not contribute much to the energy transfer process, if it exists at all, within the present systems of donor and acceptor and also due to the fact that at $R \ge 7$ Å, very weak orbital overlap may exist between the donor and acceptor concerned. So far as long-range energy transfer is concerned (which might be from singlet donor to singlet acceptor, i.e. spin-allowed transfer), actually there is no spectral argument (spectral manifestations) in favour of such transfer (though a calculated value of T, the theoretical efficiency of Förster-type energy transfer shows nearly

Table 1. Redox potential and Gibbs free energies (ΔG) for photoinduced electron-transfer (ET) processes in electron donor (THQ or THMe) and acceptor (TCNQ) systems in ACN fluid solution at 300 K

Donor	Acceptor	E ^{ΟX} † (V)	$E_{1/2}^{\text{RED}}$ † (V)	E _{0.0} * (eV)	ΔG (eV)
THQ	TCNQ	0.6	-0.35		0.95
THMe	TCNQ	0.62	-0.35		0.97
'THQ*	TCNQ			4.05	- 3.10
'THMe*	TCNO			4.04	- 3.07
тно	¹ TCNQ*			2.92	- 1.97
THMe	¹ TCNQ*			2.92	- 1.95

* Denotes excited state S_1 .

† Values are obtained in ACN vs SCE.

Table 2. Fluorescence lifetimes (r) of the donors (THQ or THMe) in binary (ACN) and ternary (ACN + TCNQ and ACN + HQ) solutions and measured k_{ET} electron transfer rates for the systems THQ + TCNQ and THMe + TCNQ in ACN fluid solutions at 300 K

Solvent	Systems	τ (±0.04) (ns)	$k_{\rm ET} imes 10^{7}$ † (s ⁻¹)
ACN	'THQ*	4.20	
	¹ THQ* + TCNQ	$3.80(\tau_1)$	2.51
	¹ THQ* + HQ	$4.20(\tau_2)$	
	¹ THMe*	4.26	
	¹ THMe* + TCNQ	$3.81(\tau_1)$	3.00
	¹ THMe* + HQ	4.30 (r ₂)	

* Denotes the electronic excited state S_1 .

 $\dagger k_{\rm ET}$ values have been evaluated from the relation $k_{\rm ET} = 1/\tau_1 - 1/\tau_2$ (see text).

100% efficiency). This observation was contrary to our expectation because if such energy transfer occurs, the acceptor fluorescence should be sensitized, especially in the case of the acceptor TCNQ which fluoresces. All the results discussed so far in the present investigation lead to the idea that in the present systems of donor and acceptor, mainly the photoinduced ET process has the major role in deactivating nonradiatively the S_1 state of donor molecules. Thus, even when the donor is excited, only ET mechanisms are found to be responsible for the observed quenching of donor fluorescence in the presence of the acceptor TCNQ. Hence from the quenching of fluorescence lifetime of the donor (which might be, as discussed above, due only to ET reactions between donor and acceptor molecules) in the presence of the acceptor, the electron transfer (ET) rate constant, $k_{\rm ET}$ has been estimated. The procedures are discussed below in detail.

Time-resolved spectroscopic measurement in the time domain of nanosecond order

At 300 K in ACN fluid solution only a single fluorescence lifetime is obtained both in the case of THQ (4.2 ns) and THMe (4.3 ns), both being served as donors in the present investigations. This shows methyl substitution does not affect the fluorescence lifetime of the present donors. When the donor THQ or THMe chromophore is excited ($\lambda_{exc} \sim 306$ nm) the fluorescence decay of the mixture of THQ (or THMe) and TCNQ in the same ACN solution retains the nature of a single exponential, but deconvolution analysis of the decay shows the decrease of fluorescence lifetime of the donor in the presence of the acceptor (Table 2). Considering (as all evidence obtained from steady state measurements are in favour of ET reactions) the reduction of fluorescence lifetime of the donor (Table 2) results from ET reactions with the acceptor TCNQ, we evaluated k_{ET} from the following relation [50, 51]:

$$k_{\rm ET} = \frac{1}{\tau_1} - \frac{1}{\tau_2}.$$
 (3)

The relation (3) is valid on the condition that back electron transfer i.e. geminate recombination to the ground state, can be neglected [51(b)]. The observed results from the steady state fluorescence measurements, discussed above, indicate that the dissociation rate of the geminate ion pair complex is much larger than the rate of charge recombination for the present donor-acceptor systems. Thus, relation (3) seems to be valid for the present donor-acceptor systems. In relation (3) τ_1 and τ_2 are the fluorescence lifetimes of the donor, respectively, with and without quenching. τ_2 is usually

measured by changing the acceptor for a molecule posessing similar structure to that of the acceptor but which does not take part in ET reaction with the donor chromophore. By using a particular concentration of the donor and acceptor ($\sim 10^{-4}$ mol dm⁻³) in ACN solvent we have measured $k_{\rm FT}$ (from τ_1 and τ_2 values). As reported by some earlier authors [23], in such a dilute solution of donor and acceptor the value of R, centre-tocentre distance between the donor and the acceptor, could be assumed to be nearly 7 Å. In the present investigation, hydroquinone (HQ), which does not undergo ET reaction with the donor, has been used in measuring r_2 . From Table 2, it could be seen that the fluorescence lifetimes of the donor molecules in ACN fluid solution at 300 K do not alter at all with the addition of HQ. Use of HQ to measure $k_{\rm ET}$ was reported by earlier authors [51]. The above findings also corroborate our proposition made from the steady state measurements that in the presence of TCNQ the photophysical changes occurring in the donor are mainly due to electron transfer reactions. Energy transfer, if it exists at all, has a minor role in the quenching mechanism of donor fluorescence in ACN solution at 300 K. Values of τ_1 , τ_2 and $k_{\rm ET}$ for the systems of excited donors and ground state acceptor are shown in Table 2. From the large negative value of ΔG (~-3.10 eV) coupled with low values of $k_{\rm ET}$ for the system of THQ*-TCNQ or THMe*-TCNQ (* denotes excited state S_1) (Table 2), it seems the reaction occurs in a highly exothermic region and might possibly be in the Marcus inverted region where outer-sphere ET for producing a radical ion-pair might not be fast. If one compares ET rates, as shown in Table 3 of the systems ¹THQ*-TCNQ, ¹THMe*-TCNQ and ¹Xylenol*-TCNQ (ET results from this system have been reported in our previous communication [32]) it will be seen that with increase of exothermicities (more negative values of ΔG), the ET rate has a tendency to decrease. These results are an experimental demonstration of the energy gap dependence of the ET (charge separation) rates resulting from photoinduced electron transfer reaction in the Marcus inverted region. However, to prove conclusively the fact of the ET reaction occurring in the Marcus inverted region, more investigations should be carried out as the values of $k_{\rm ET}$ do not differ much in the cases of donor-acceptor pairs presented in Table 3.

The above studies show that when the donor or acceptor chromophore in ACN solution is excited, a highly exothermic electron transfer reaction might occur (from large negative ΔG and low k_{ET} values) possibly in the Marcus inverted region. Initially this reaction, in all probability, generates a transient radical ion-pair in the excited state which dissociates gradually in ACN fluid solution producing more and more TCNQ⁻ ion as evidenced from: (1) enhancement of fluorescence emission of this ionic species (Fig. 3) when the acceptor chromophore is excited; and (2) appearance of a weak fluorescence band at the 432 nm region when the excited donor undergoes ET reaction with the acceptor TCNQ. Following the view of MATAGA *et al.* [23] it might be argued that in ACN fluid solution due to the excitation of the acceptor or donor chromophore a geminate ion-pair complex of loose structure is formed and due to this structural property rapid dissociations into radical ions result.

Table 3. Comparison between ΔG and k_{ET} values to demonstrate energy gap dependence of electron transfer rate in cases of some donor acceptor pairs

Donor	Acceptor	ΔG (eV)	$\frac{k_{\rm ET} \times 10^7}{({\rm s}^{-1})}$
'THQ*	TCNQ	- 3.10	2.51
¹ THMe*	TCNQ	- 3.07	3.00
¹ Xylenol*†	TCNQ	-2.47	4.40

* Denotes the electronic excited state S_1 . † Ref. [32].

CONCLUSIONS

Investigations by steady state fluorescence spectra reveal the formation of a transient CIP (or geminate ion-pair) complex in the excited state, followed by dissociation into radical ions when the excited donor (or excited acceptor) undergoes ET reaction with the ground state acceptor (or donor). These observations seemingly indicate that the transient geminate ion pair complex formed due to ET reaction possesses a loose structure which easily dissociates to form stable ionic species in highly polar and ionizing solvent ACN. Interestingly this phenomenon observed in the present investigation contrasts with that of the chlorophyll a-benzoquinone (BQ) or bacteriophephytin-BQ systems where solvated radical ions or ET states produced from the S_1 state were not detected even by picosecond spectroscopy [52].

The low values of k_{ET} coupled to large negative values of ΔG (especially when the donor chromophore is excited, Tables 1 and 2) indicate that the ET reaction might occur in the highly exothermic region and most probably in the Marcus inverted region.

It is suggested that in the present systems of donors and acceptors, quenching observed in fluorescence emission of donor molecules is caused primarily due to outer-sphere ET, the centre-to-centre distance between donor and acceptor being ca 7Å. It is also suggested that at such a long distance between donor and acceptor, the geminate ion-pair becomes the secondary quenching product since the outer-sphere ET can induce quenching at such a long distance.

It seems in the present system of donors and acceptor only one process (the ET process) is responsible for the observed quenching of donor fluorescence.

All these observations lead to the idea that with the help of these donors and the TCNQ acceptor, some bichromophoric systems could be developed by connecting donor and acceptor through spacers of polymethylene type (σ -spacer) or carotenoid (π -spacer) type to build good photoconducting materials. Syntheses of such novel systems are now underway in our laboratory.

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