Magnetic Field Effect: A Tool for Identification of Spin State in a Photoinduced Electron-Transfer Reaction

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The present work addresses the investigation of the influence of substitution on the initial spin state in photoinduced electron-transfer (PET) reactions with a series of four exciplex systems i.e., *N*-ethylcarbazole (ECZ)−1,4-dicyanobenzene (DCB), 1,4,5,8,9-pentamethylcarbazole (PMC)−DCB, ECZ−1,2,4,5-tetracyanobenzene (TCNB), and PMC−TCNB by means of a low magnetic field (MF) (0.05 T). The two primary intermediates that play major roles in determining the efficiencies of bimolecular PET reactions are the contact ion pair (CIP), i.e., (A^-D^+), and the solvent-separated ion pair (SSIP) ($A^-(S)D^{\bullet+}$). The effect of MF of the order of hyperfine interaction present in the system on such reactions reflects the unique combination of spin dynamics, diffusion dynamics, and geminate recombination in the SSIPs. Thus MF can be successfully used to investigate the initial spin state of a SSIP where electronic coupling between acceptor (A) and donor (D) molecules is small indeed. The experimental techniques have used either laser flash photolysis to estimate the magnetic field effect (MFE) on triplet free ions or an improved phase-sensitive detection system to measure the enhancement in singlet CIP or exciplex luminescence. By the changes of the substituents in A/D molecules, the modifications in the production of either singlet or triplet SSIPs have been discussed. The observed MFEs have been correlated with the Marcus relation between free energy changes and redox potentials. Another novel finding is that MFE on exciplex luminescence is controlled not only by the dielectric of the medium but the extent of electronic coupling, i.e., the extent of charge transfer (δ), between D and A molecules also plays a major role in it. The deviation in $\epsilon_{\max}$, the dielectric for maximum MFE, from the previously obtained values has been discussed on the basis of the modification in the potential energy surfaces between CIP and SSIP, which has been further supported by an analytical model.

1. Introduction

The mechanism and dynamics regulating a photoinduced electron-transfer (PET) reaction in liquid solutions, rigid matrices, molecular assemblies, and biological systems are the most fundamental problems in the photophysical and photochemical primary processes.[1−10] Along with the studies of the electron-transfer (ET) mechanisms in the fluorescence quenching between uncombined donor and acceptor, exciting advances have been made due to the remarkable development in experimental methods such as ultrafast laser spectroscopy. The identification of the transient species formed by light absorption is necessary for elucidation of the reaction mechanism and to govern a reaction as desired. It reveals that the fate of a PET reaction depends mainly on the spin state of the transients produced initially after excitation. For example, if ET takes place between a donor (D) and an acceptor (A) molecule in singlet spin state, radical ion pairs (RIPs) are also in singlet states that form cage products, i.e., contact ion pair (CIP) or exciplex, whereas ET in the triplet state leads to the formation of escape products or free ions that are highly reactive. Therefore, if an equilibrium exists between singlet and triplet RIPs, formation of different types of products are possible. During last two decades it has been observed that the application of a low magnetic field (MF) on this ET process[11−28] has remarkable potential in identification of original spin states of the RIPs as well as in controlling the production of cage/escape products by modulating the spin states, i.e., by disturbing the existing equilibrium between the singlet and triplet states. If it is assumed that RIPs are formed initially in the singlet state, equilibrium will exist between a singlet and three degenerate triplet states. This singlet−triplet (S−T) conversion is mainly caused by the hyperfine interaction (HFI) present in the system. Application of an external MF that can overcome the HFI will reduce S−T transition by inducing a Zeeman splitting in the triplet states resulting in T_+ and T_- nondegenerate with respect to T_0. Therefore, on introduction of a MF, the yield of a singlet cage product increases almost by two-thirds of that in the absence of an external MF. By the same analogy, when RIPs form initially in the triplet state, on the application of a MF, the triplet yield, i.e., free ion formation, increases. There are many examples where it has been cited that singlet exciplex luminescence[18−23] increases even by 10% in the presence of an external MF. On the other hand, many other examples are also there, where free ion formation is enhanced in the presence of a MF from the initially formed triplet RIPs.[12−17,24−28]

Here arises an important question of whether it is possible to alter the primary ET reaction pathways by changing the substituents of D−A molecules. In this paper we report a comparative study between D−A systems that consist of two derivatives of carbazole, i.e., *N*-ethylcarbazole (ECZ) and 1,4,5,8,9-pentamethylcarbazole (PMC) as donor molecules and a pair of cyanobenzenes, i.e., 1,4-dicyanobenzene (DCB) and 1,2,4,5-tetracyanobenzene (TCNB), as acceptor molecules to observe the effect of substitution on a PET reaction. For this

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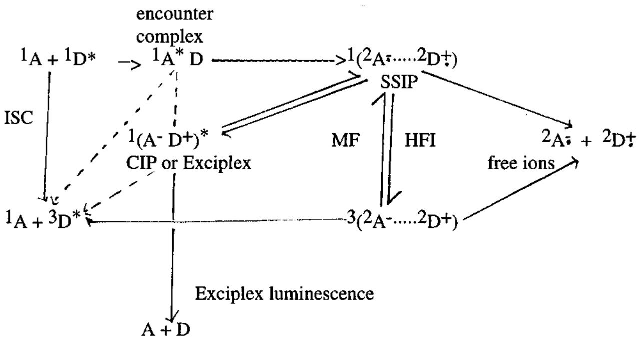
SCHEME 1



investigation we have chosen an external low MF as a tool that can successfully identify the particular spin state for the ET process. This phenomenon would be very useful in practical sciences. For example, drug designing is one of the fascinating fields of research today, and this knowledge may provide effective guidance to prepare new drugs where a particular design is required.

Previously, we reported an ET reaction between ECZ and DCB that also leads to an exciplex formation.[17] In that communication, we cited the identification of the parent spin state of the RIP by laser flash photolysis in the absence and presence of an external MF. There, the initial part of the triplet decay curve, which is mainly due to the formation of DCB^- decaying faster than that of ECZ alone, is affected by MF. The result satisfies Scheme 1, which depicts that the geminate RIP initially forms in the singlet spin state. Therefore, on the application of a MF, the triplet yield of free ions decreases. In another communication the prediction about the initial spin state of this RIP has been further verified by monitoring the magnetic field effect (MFE) on exciplex luminescence directly using an improved phased-sensitive detection (PSD) system.[23] The exciplex luminescence, i.e., singlet CIP yield, increases in the presence of a MF, which supports the origin of RIPs in the singlet spin state. Using the results of ECZ−DCB exciplex system as background information, we have attempted to replace the D/A molecules with their other derivatives to see whether the substituent can modulate the course of the reaction and MF is really an efficient tool to identify the initial spin states of RIPs.

It is known that MF on RIPs is an interplay of spin dynamics and diffusion dynamics. Diffusion of the partners of the RIPs provides the necessary time to separate the ions at a distance where exchange interaction (J) between the partners becomes negligible and spin evolution can take place, which enhances either geminate recombination or formation of the free ions. The polarity of the medium plays a major role in controlling the diffusion dynamics of the RIPs. In an extremely nonpolar medium most of the RIPs recombine at once whereas in an highly polar medium free ion formation predominates and both the processes are reluctant to respond to an external MF. Therefore, the MF maximizes at an intermediate dielectric constant (d.c.).[19−23] This variation of d.c. on MF can be identified in a better way only in exciplex systems. From the earlier works with different types of exciplex systems, it was accepted that irrespective of the exciplex the effects would maximize at ϵ (ϵ_{max}) within the limit $14 < \epsilon < 18$ for different choice of components of aprotic solvents after the onset at $\epsilon \approx 9$. Very recently we have shown that this particular limit does not hold for all the exciplex systems. In the ECZ−DCB exciplex system ϵ_{max} has been found to be almost equal to 9, which is far lower than the previous limit with the onset around $\epsilon \approx 6$.[23] Therefore, it has been concluded that the polarity of the medium does not solely control the maximum field effect but the nature and the extent of charge-transfer character of the exciplex system also play major role since these factors bring a significant change in the ϵ_{max} value to optimize the effect. In this paper we have also verified our argument by comparing the ϵ_{max} between the two derivatives of carbazole and DCB systems where the nature of exciplex and the extent of charge transfer are quite different from each other.

2. Experimental Section

Materials. ECZ, PMC, and DCB were purchased from Aldrich and TCNB from Fluka. Spectroscopic grade tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF) and acetonitrile were used after proper distillation. Sodium dodecyl sulfate (SDS) was purchased from Sigma.

Apparatus. Triplet spectra and lifetimes were measured using a nanosecond flash-photolysis setup (Applied Photophysics) containing an Nd:YAG (DCR-11, Spectra Physics). The sample was excited by 355 nm laser light (fwhm = 8 ns) Triplet species were monitored through absorption of light from a pulsed xenon lamp (250 W). The photomultiplier (1P28) output was fed into a storage oscilloscope (TDS-540 Tektronix, 500 MHz, 1 giga sampling, Gs, S^{1-}), and stored data were subsequently transferred to a computer through a GPIB/IEEE interface. The MFE was studied by inserting a pair of electromagnetic coils inside the sample housing as shown elsewhere.[17] The decay constants have been evaluated with the help of a standard program for a least-square fit of a sum or difference of two exponential functions with a linearity of the fitting function using a MARQUADT nonlinear search algorithm[29.]

A homemade full-wave phase-sensitive detection (PSD) system was used to study the dependence of steady-state singlet luminescence on MF.[15a,23] The magnet with the sample cuvette between the poles has been placed inside the commercial nanosecond laser flash photolysis chamber, and the sample has been excited transversely by the UV light (using IR and visible cutoff filters (Oriel: 52190 and collimating optics) of a current-stabilized 250 W xenon lamp. The luminescence has been collected through a small hole in one pole of the magnet by the conventional double-lens optics and the monochromator of the chamber and is detected by a 1P28 photomultiplier biased for low-current, high-gain operation with a load impedance of 1 MΩ. The details have been given earlier.[23]

The solutions were deaerated using pure argon for ca. 40 min before measurements.

The oxidation potential value (E_{ox}) of the PMC is the half-wave potential measured by a cyclic voltameter (EG & G Princeton Applied Reasearch, Model 372) in polar aprotic solvent (0.1 N tetrabutylammonium perchlorate in acetonitrile) in volt vs SCE. The E_{ox} value of PMC was measured as 1.0 eV.

3. Results

(a) MFE on Triplet RIPs by Laser Flash Photolysis. Figure 1 shows the transient spectra of ^{3}PMC in the presence and absence of DCB or TCNB. The spectrum of ^{3}PMC shows the maximum absorption at 400 nm, whereas in the presence of DCB and TCNB new humps appear at 430 and 465 nm which are due to the absorption of DCB[16,17] and TCNB[30] anions, respectively. Figure 2 shows the decay profile of ECZ−DCB and PMC−DCB whereas Figure 3 shows those of ECZ−TCNB

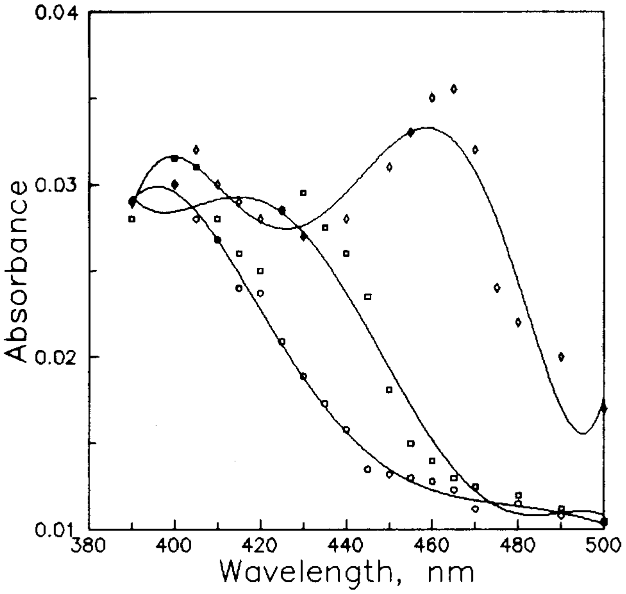


Figure 1. Transient spectra of ^{3}PMC (○) (1.0×10^{-5}mol dm^{-3}) in the presence of DCB (□) (2×10^{-3}mol dm^{-3}) at a delay of 0.12 μs and TCNB (◇) (2×10^{-4} mol dm^{-3}) at a delay of 1 μs in 10% SDS micellar medium.

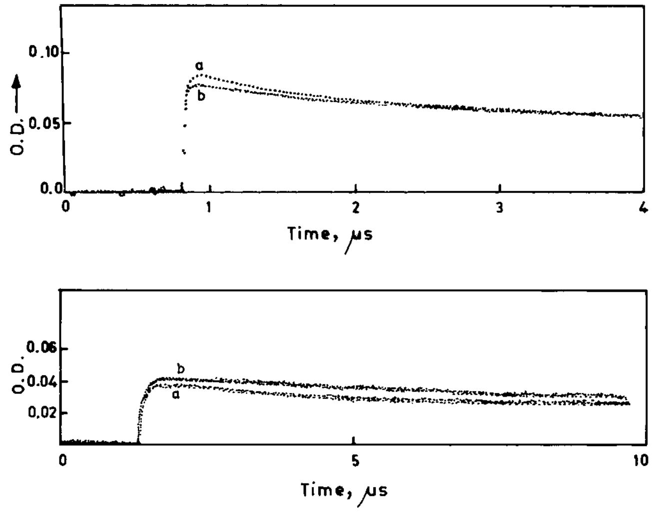


Figure 2. Decay profiles of (i, top) ECZ (1.3×10^{-4}mol dm^{-3})−DCB (2×10^{-2} mol dm^{-3}) and (ii, bottom) PMC (1.3×10^{-4}mol dm^{-3})−DCB (2×10^{-2} mol dm^{-3}) in 10% SDS micellar medium at 430 nm in (a) the absence and (b) the presence of a MF of 0.05 T.

and PMC−TCNB in the absence and presence of MF. The corresponding decay rate constants that are the inverse of the average lifetime of the transients are depicted in Table 1. The change in decay profile in the presence of MF is just the opposite in ECZ−DCB compared to PMC−DCB systems. In the former, MF accelerates the decay rate, i.e., decreases the lifetime of the transients, whereas in the latter, the decay rate constant decreases in the presence of MF, which means the lifetime of the transient increases. But when DCB is replaced by TCNB, i.e., in ECZ−TCNB and PMC−TCNB systems, the decay rates become much slower in both the cases, which means the lifetimes of the corresponding transients are quite enhanced in the presence of the MF. The differences between the absorbance values of the transients in the presence and absence of MF in ECZ−TCNB and PMC−TCNB systems have been plotted against corresponding wavelengths (Figure 4). This depicts that the yield of TCNB$^-$ at 465 nm[30] as well as the ^{3}ECZ* and ^{3}-PMC* at 400 nm increase in the presence of a MF.

(b) MFE on Exciplex Luminescence Using the PSD System. Figure 5 shows the effect of the MF on exciplex luminescence with variation of wavelength for ECZ−DCB system. Table 2 describes the maximum change in exciplex luminescence, $\Delta\phi/\phi$%, where $\Delta\phi$ is the change in the initial exciplex luminescence, ϕ in the presence of MF and $B_{1/2}$ values are the HFI present in the ECZ−DCB and PMC−DCB systems. $B_{1/2}$ values remain invariant with DCB concentration. The field effect on luminescence maximizes at the peak of the exciplex, which shows that only the exciplex is affected by MF.

Figure 6 represents the change in exciplex luminescence in the presence of MF with the d.c. of the medium. Here only the mixtures of aprotic solvents have been used. In ECZ−DCB, the maximum field effect attains at the d.c. ($\epsilon_{\max}$) at 9.0 with the onset at 6.0 whereas in PMC−DCB, $\epsilon_{\max}$ shifts to higher ϵ, i.e., $\epsilon_{\max}$ 12.0, with the ϵ starting around 9.5. The theoretically fitted curves according to the analytical expression based on Smoluchowski's diffusion equation have also been shown in the Figure 6 to compare the experimental results.

In case of ECZ−TCNB and PMC−TCNB systems, because of the nonexistence of exciplex, there is no need to study the MFE on exciplex luminescence.

4. Discussion

In accordance with the spin state a bimolecular PET reaction may be classified as an ET either in the excited singlet state or in the excited triplet state. The MFE influencing directly the rate of multiplicity conversions of the RIPs may affect several channels: formation of free radicals or locally excited triplet states and exciplex luminescence. The modulation of spin dynamics of RIPs in solution can be detected either by using the laser flash photolysis technique on the triplet nonfluorescent precursors in micellar medium or by monitoring the increase in exciplex luminescence of the singlet precursors in homogeneous solutions. Micelles provide a heterogeneous medium where not only the partners of the geminate RIPs get sufficient space to be separated out from each other at a distance where J is negligible but also the lifetime of the transients become much longer compared to that in homogeneous solution; henceforth, MFE can be studied in more detail in micellar medium. The most interesting and important feature of the systems studied here is that the photoexcitation can produce both the singlet as well as the triplet excited states by rapid intersystem crossing (ISC) and thus ET can take place from both the excited states. The percentage of RIPs formed in either of these two states depends on the substitution in the fluorophores or in the quenchers. From the variation of decay rate constants (Table 1) in the absence and presence of MF, one can assess the spin state of the parent RP/RIP from which the particular transients have originated. In the case of the ECZ−DCB system, the acceleration of the triplet decay rate with a maximum at 430 nm implies the decrease in triplet yield of free DCB$^-$.[16,17] Therefore, in this case, the formation of RIP occurs initially in the singlet state as discussed earlier.[17] This conclusion has been further supported by the enhancement of exciplex luminescence by steady-state MFE.[23] When ECZ has been replaced by another derivative of carbazole with a greater number of substituents, i.e., PMC, the yield of triplet DCB$^-$ increased in the presence of a MF, which is just reverse of the former results obtained in ECZ−DCB. Therefore, it can be interpreted that in PMC−DCB the RIPs have been originated in the triplet state. On the other hand, the steady-state MF experiments on PMC−DCB have shown very little increase in exciplex luminescence in the presence of a MF, which might

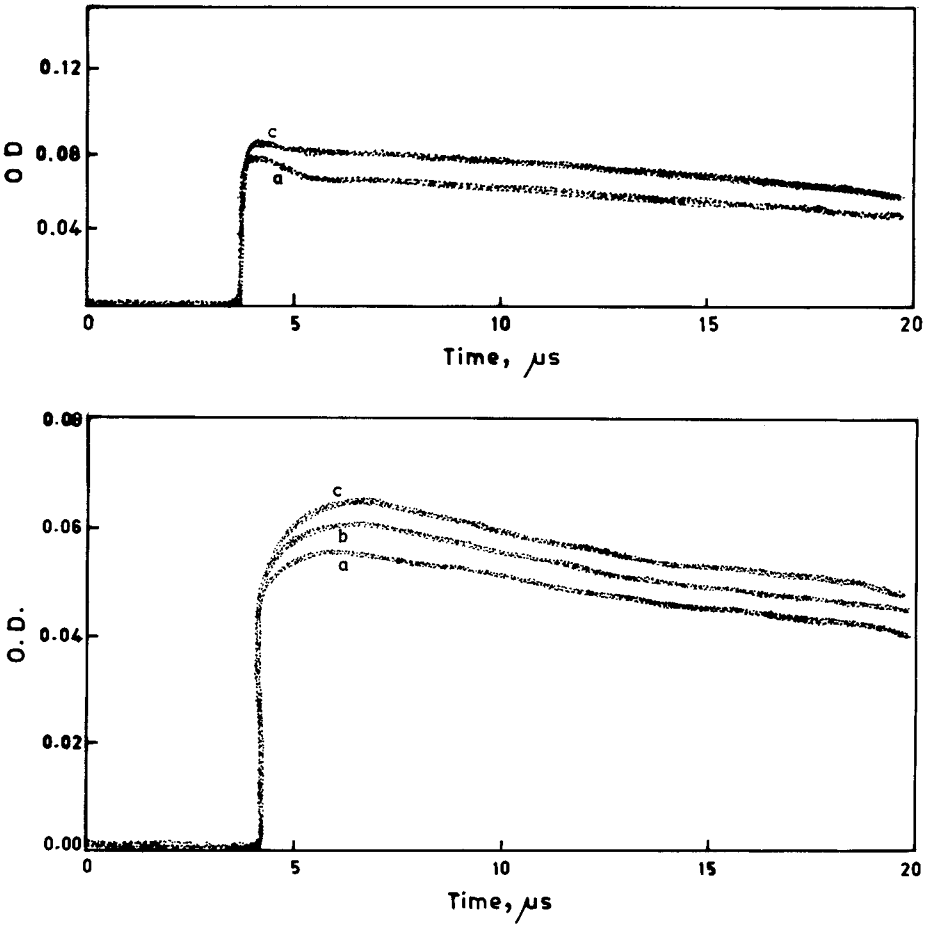


Figure 3. Decay profiles of (i, top) ECZ (5.0×10^{-5} mol dm^{-3})−TCNB (4×10^{-4} mol dm^{-3}) and (ii, bottom) PMC (5.0×10^{-5} mol dm^{-3})−TCNB (4×10^{-4} mol dm^{-3}) in 10% SDS micellar medium at 465 nm in the presence of MF of (a) 0.0 T, (b) 0.02 T, and (c) 0.05 T.

TABLE 1: MFE on the Decay Rate Constants (k)[a] for Four Pairs of D/A Systems in SDS Micellar Medium

acceptor/	DCB, $k \times 10^5$ (s^{-1})		TCNB, $k \times 10^4$ (s^{-1})	
donor	0 T	0.05 T	0 T	0.05 T
ECZ	6.1 ± 0.03	6.9 ± 0.02	2.25 ± 0.03	1.65 ± 0.02
PMC	1.0 ± 0.025	0.92 ± 0.03	1.95 ± 0.03	1.31 ± 0.02

[a] Decay profiles consist of two parts. The decay rate constants for short-lived species, i.e., for DCB$^-$ and TCNB$^-$, corresponding to the initial part of the respective decay curves showing a significant change in the presence of MF[17] are given here.

come from a very small amount of RIPs that originated in the singlet state. Therefore, there exists a dual behavior in PMC−DCB that might be explained if it is considered that due to the increase in the number of substituents in the carbazole, ISC from S−T of excited PMC is enhanced significantly. It signifies that the probability of formation of RIP in both the singlet and triplet spin states in PMC−DCB is competitive. It is known that a triplet state consists of three degenerate states whereas a singlet contains only one; therefore, if the singlet yield is changed by one-third of the initial, the corresponding triplet yield will be changed by two-thirds of that. Hence, in the PMC−DCB system as there exists a competition between the singlet and triplet RIP yields, the singlet is modulated only by 0.025% whereas the triplet by 7%, which means change in triplet yield is much more prominent compared to that in singlet yield. Thus Scheme 1 needs some modifications which are shown in Scheme 2[11b] by dotted lines.

Striking results are obtained when DCB has been replaced by other cyano derivatives with more cyanide groups than DCB, i.e., TCNB. In this case triplet yield of TCNB$^-$ which maximizes at 465 nm, is markedly enhanced both in ECZ−TCNB and PMC−TCNB systems in the presence of MF. Here, TCNB, through its four −CN groups, induces ISC faster in both systems owing to spin−orbit coupling in the encounter complex, and ET takes place between fluorophore and TCNB in the triplet state.[31] Therefore, exciplex luminescence cannot be observed in ECZ−TCNB and PMC−TCNB as we have mentioned before.

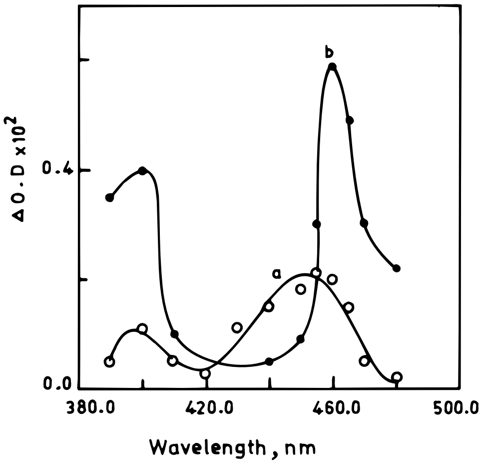


Figure 4. Variation in absorbance of the transients ΔOD, in the presence of a MF (0.05 T) and absence of a MF for (a) ECZ (5.0×10^{-5} mol dm^{-3})−TCNB (4×10^{-4} mol dm^{-3}) (○) and (b) PMC (5.0×10^{-5} mol dm^{-3})−TCNB (4×10^{-4} mol dm^{-3}) (●) with wavelength (λ) in 10% SDS micellar medium at a delay of 1.0 μs.

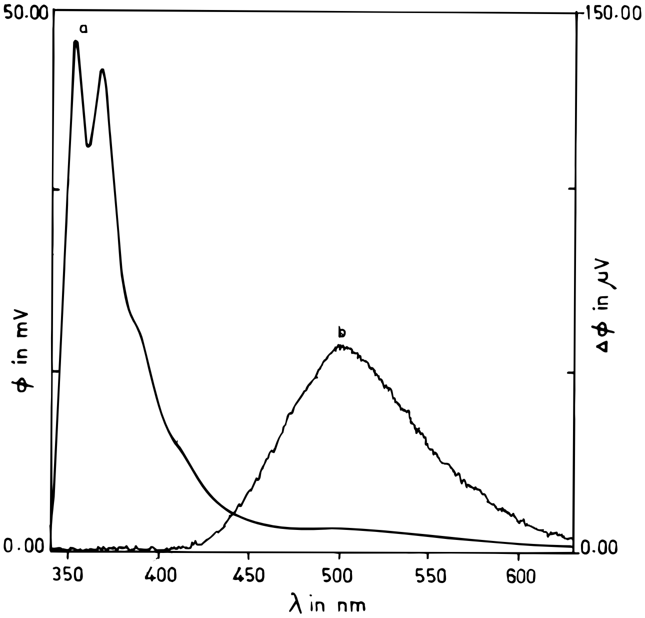


Figure 5. Variation of (a) luminescence ϕ (in mV) and (b) change in luminescence $\Delta\phi$ (in mV) with λ in the presence of saturating MF of 0.012 T for ECZ (2×10^{-4} mol dm^{-3})−DCB (3×10^{-2} mol dm^{-3}) at $\epsilon = 9$ in THF−DMF mixture.

TABLE 2: $\Delta\phi/\phi$% and $B_{1/2}$ Values for ECZ−DCB and PMC−DCB from MF-Modulated Luminescence Experiments[a]

system	$\Delta\phi/\phi$%	$B_{1/2}$ (G)
ECZ−DCB	1.37	32
PMC−DCB	0.025	43

[a] Concentration (mol dm^{-3}) of the fluorophore:quencher = 2×10^{-4}: 3×10^{-2}.

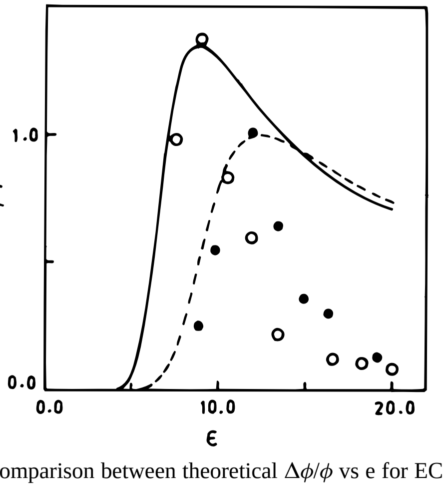
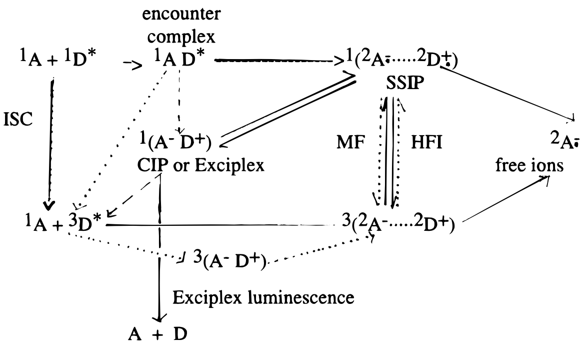


Figure 6. Comparison between theoretical $\Delta\phi/\phi$ vs e for ECZ−DCB (solid line —) and PMC−DCB (dashed line − - −) with their corresponding experimental data points (○) and (●), respectively, in THF/DMF mixed solvent. The data for PMC−DCB are magnified by 40 times. The values of the parameter for the theoretical curve: $\alpha = 45\,000$, $r_g = 8$ Å,[22f] $R = 7$ Å for ECZ−DCB and $\alpha = 4500$; $r_g = 8$ Å, $R = 6$ Å for PMC−DCB.

It is really interesting to correlate the free energy ($\Delta G°$) dependence with MFEs on RIPs.[16] This may provide a deeper insight into PET reactions. Marcus[32] and Rehm-Weller[33] proposed an equation that correlates the rate of an ET with corresponding free energy changes. The general equation for forward ET is $\Delta G_f° = E_{ox} - E_{red} - E_{0-0} - C$ and for back-ET $-\Delta G_b° = E_{ox} - E_{red} + C$. The term C is the Coulombic interaction, which is equal to $e^2/\epsilon r$, where e is the electronic charge, ϵ is the dielectric constant of the medium, and r is the interionic distance. In acetonitrile C is less than 0.06 eV where r is more than 7 Å. Therefore, C can be neglected in acetonitrile.[3a] Let us apply this equation in the first two pairs where only the fluorophore has been changed, keeping the quencher unaltered, e.g., in ECZ−DCB and PMC−DCB systems. For ECZ−DCB $\Delta G_f° = -0.83$ eV and $-\Delta G_b° = 2.77$ eV, ($E_{ox} = 1.12$ eV for ECZ;[17,34] $E_{red} = -1.65$ eV for DCB[16,17,34]), whereas for PMC−DCB $\Delta G_f° = -0.89$ eV and $-\Delta G_b° = 2.65$ eV ($E_{ox} = 1.0$ eV for PMC). Thus from the free energy changes it is clear that forward ET is more in case of PMC−DCB as $\Delta G_f°$ for PMC−DCB is greater than that of ECZ−DCB. This result has also been supported from the Stern−Volmer quenching rate constant obtained from both the steady-state and time-resolved studies ($k_q^{ECZ-DCB} = 25.2 \times 10^9$ mol dm^{-3} s^{-1} and $k_q^{PMC-DCB} = 31.3 \times 10^9$ mol dm^{-3} s^{-1} in acetonitrile at 25 °C). On the other hand, following the same argument the back-ET predominates in ECZ−DCB compared to PMC−DCB. The two primary intermediates that play major roles in bimolecular PET reactions are the CIP and SSIP. These two species are distinguished by the differences in electronic coupling, which is much smaller for SSIP compared to CIP, and solvation, which is much larger for the SSIP compared to CIP. The weak electronic coupling in the SSIP results in a very small singlet−triplet energy gap, so that the ISC between spin states can be modulated by the application of a weak MF. Since the back-ET recombines the SSIP/CIP to the ground state, the greater the forward reaction, the greater the MFE. Therefore, it is expected that for PMC−DCB the MFE will be more pronounced compared to that for ECZ−DCB. But actual findings contradict the prediction. The $\Delta\phi/\phi$% value for PMC−DCB is much less (more than 40 times) compared to that for ECZ−DCB. It may happen because the ISC of ^{1}PMC* to ^{3}PMC* is very efficient as shown in Scheme 2. Moreover, the singlet quantum yield of ECZ is 0.92, whereas that for PMC is only 0.58. So the ET from both ^{1}PMC* and ^{3}PMC* are in competition with each other, which has been discussed earlier. This relation between free energy and MFE also tallies well with the experimental observation for the other pair of the present systems, ECZ or PMC with TCNB.

SCHEME 2



The $B_{1/2}$ value is the measure of HFI present in the system.[22,34] A quantitative co-relation of $B_{1/2}$ with the hyperfine interaction energy of the individual radical pair B_i was established by Weller et al.[34] as follows

$$B_{1/2} = 2(B_1^{\,2} + B_2^{\,2})/(B_1 + B_2)$$

The individual B_i values can be calculated by the following expression

$$B_i = \left(\sum a_{iN}^{\,2} I_N(I_N + 1)\right)^{1/2}$$

on the basis of interaction between nuclear spin I_N and the unpaired electron spin in each radical, which governed by the isotropic hyperfine coupling constant a_{iN} (values obtained from ESR). So, to estimate the theoretical $B_{1/2}$ values the required parameters are the a_{iN} values for ECZ, PMC, and DCB. Unfortunately the a_{iN} values for ECZ and PMC are not available. To make a comparison, 3,6-dimethylcarbazole (DMC) has been chosen as a reference system whose a_{iN} values are known[35] ($B^{DMC} = 19.3$ G and $B^{DCB} = 4.6$ G[13e]). The $B_{1/2}$ values for ECZ−DCB and PMC−DCB obtained from MF-modulated luminescence experiment have been shown in Table 2. The experimental results show good resemblance to theoretically calculated values from the similar type of system. Moreover, the one unique observation is that the $B_{1/2}$ values remain invariant with respect to increase in DCB concentration for ECZ−DCB and PMC−DCB systems. So far, in other exciplex systems, pyrene-*N*,*N*-dimethylaniline (Py−DMA), 9-cyanophenanthrene−*trans*-anethole (CNP−AN), etc., the $B_{1/2}$ value increases with quencher concentration.[15c,22b] In the above exciplex systems, the major contribution comes to the HFI from the quencher whose concentrations are normally varied to obtain more exciplex luminescence. Therefore, increase in DMA or AN concentrations results in the lifetime shortening of a particular RIP due to electron hopping from one quencher to other quencher leading to a broadening in the S−T energy levels. Therefore, to overcome this energy broadening more field is required to get the saturation; hence, $B_{1/2}$ increases. But in the present case, maximum contribution to HFI originates from the fluorophore itself, i.e., ECZ or PMC, and not from the DCB molecules. Therefore, on increasing DCB concentration, although the electron hopping between DCB$^-$ cannot be restricted, there is no change in the $B_{1/2}$ value. Here, the concentration of the flurophores, major contributors to the HFI, is kept fixed at the order of 10^{-4} M. A small change in fluorophore concentration may not result any change in $B_{1/2}$ as in this low concentration electron hopping is overruled. Moreover, it would be rather difficult to design any spectroscopic experiment where the concentration of the fluorophore could be increased to such an extent to make the electron hopping effective.

The results obtained from the effects of d.c. on the relative MF-induced change in the exciplex luminescence for ECZ−DCB and PMC−DCB systems are really very unusual but interesting. So far, the existing idea on the magnetic field modulated emission of the exciplex, originated from the SSIP, shows that the maximum field effect attains within a particular range of d.c., which is $14 < \epsilon_{max} < 18$ for aprotic solvent mixtures.[19−23] Chowdhury and his co-workers[22] found that for various neat and mixed aprotic solvents, the increase in exciplex luminescence yield reaches a maxima near a solvent d.c. of 16 on application of a saturating MF. Petrov et al.[19] invoked the idea of preferential solvation in a polar−nonpolar solvent mixture, and by approximate calculation they also showed that $\Delta\phi/\phi$ vs ϵ maximizes near $\epsilon = 15$. For the linked systems Basu et al.[22g] and Werner and Staerk[20a] mentioned that maximum field effect within the above-mentioned d.c. is also valid, though Tanimoto et al. and Cao et al.[18] have shown that the field effect increases monotonously by increasing the polarity of the solvent from 7 to 36 since RIPs cannot be dissociated completely into free ions. In bimolecular PET reactions normally there are three key intermediates that can be identified. These are the CIP, SSIP, and the free radical ions in solution ($A^{\bullet-} + D^{\bullet+}$) as shown in the potential energy diagram (Figure 7). The efficiency with which such reactions result in the formation of either free ions or exciplex depends upon the competition between an ET reaction and a reaction involving a change in the solvation within each of these three intermediates. The intermediates can be distinguished by their energies and the approximated center-to-center distance of the acceptor and donor. The formations of SSIP and CIP through ET are also competitive with each other. In nonpolar medium CIP formation is essentially 100% efficient since solvation to form SSIP becomes endothermic and less likely to occur. But in moderately polar medium a fraction of SSIP is converted to CIP or vice versa. There exists a potential energy barrier between SSIP and CIP that indicates the energy required to squeeze out intervening solvent molecules between the two. The remaining fraction of the SSIP can form free ions or a part of it can be geminately recombined to form SSIP again. It is considered that as the MFE on exciplex luminescence is an interplay of diffusion dynamics and the spin dynamics of the RIPs, the potential energies of the intermediates play the vital roles. The diffusion dynamics of a charged species is mainly controlled by the polarity of the solvent medium. In a completely nonpolar medium, as all the RIPs form CIP there is no effect of MF on exciplex luminescence. In a highly polar medium free ions predominate that also do not response to MFE. Only in a moderately polar medium where a fraction of singlet SSIP can be separated, spin flipped, and geminately recombined can the MFE on exciplex luminescence be detectable. Therefore, if solvent polarity is the only controlling factor for diffusion dynamics of RIPs, then ϵ_{max} should attain at that particular range of d.c irrespective of the exciplex systems. But in ECZ−DCB and PMC−DCB systems contradictory results are obtained. In ECZ−DCB ϵ_{max} occurs at 9.0, whereas in PMC−DCB it is around 12. Therefore, there should exist another factor that has significant influence on ϵ_{max} and that is probably the extent of charge transfer (δ) in exciplex systems. The CIP can be considered to be a special case of the well-known exciplex. The term exciplex is used to describe the species characterized by a wide range of mixing between ionic and locally excited states, i.e., varying degrees of charge-transfer character. When an ionic state is considerably lower in energy than the locally excited

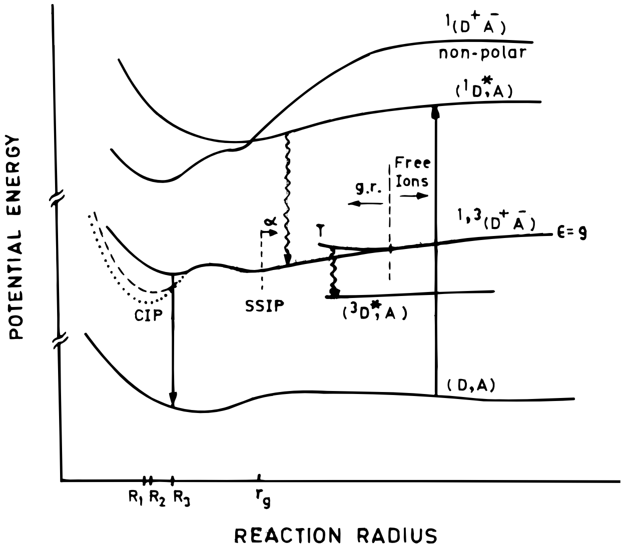


Figure 7. Schematic diagram for the potential energy (PE) surfaces of spin-dependent ET processes as a function of reaction radius in polar ($\epsilon = 9$) and nonpolar medium where CIP is contact ion pair, SSIP is solvent separated ion pair, g.r. is geminate recombination, T is triplet state, $\alpha = 10^3/h$, h is an adjustable parameter that estimates the PE difference between CIP and SSIP, solid line (—) represents the PE for ECZ−DCB, dashed line (---) for PMC−DCB, and dotted line (···) for Py−DMA assuming the PE surfaces are identical where the partners of the RIPs are at a distance for all the systems.

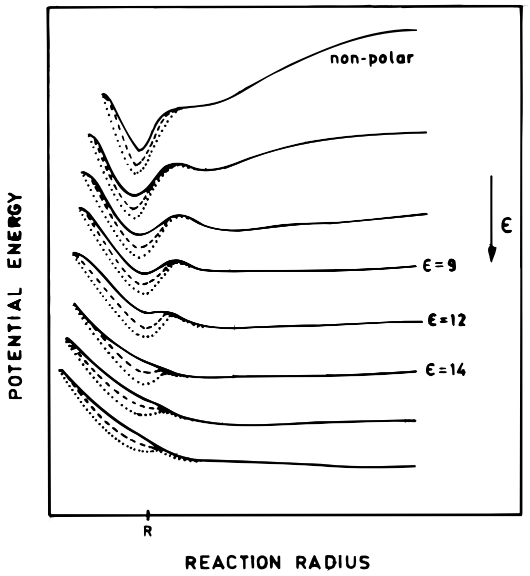


Figure 8. Schematic diagram for the variation of PE surfaces with the reaction radius with ϵ. Solid line (—) represents the PE for ECZ−DCB, dashed line (---) for PMC−DCB, and dotted line (···) for Py−DMA.

states, then very little mixing with other states will occur, and the exciplex is equivalent to a pure CIP, i.e., potential energy barrier is maximum between CIP and SSIP. In our earlier communication we reported that in ECZ−DCB δ is 0.148 compared to that in Py−DMA or Py−DEA systems where δ is equal to 1, i.e., complete charge transfer takes place.[15,23] Let us visualize the effect of on RIP potential energy surfaces (Figure 8). In the solvent of the same intermediate d.c., the less the δ, the less will be the stabilization energy of CIP due to solvation since the stabilization through solvation mainly depends on the net charges on the ion pairs.[36] Hence, the activation barrier height between SSIP and CIP would be less in ECZ−DCB compared to Py−DMA, but the potential energy surfaces between SSIP and free ions remain unaltered. This phenomenon is also reflected in the experiments where $\bar{\nu}_c$(max) of Py−DMA and ECZ−DCB have been measured in solvents of different dielectric constants[17] where it has been observed that the red shifting of $\bar{\nu}_c$(max) measuring the extent of stabilization in Py−DMA is far greater compared to that in ECZ−DCB for the same solvent variation. Therefore, in this way the activation barrier height can also be correlated with the extent of CT in exciplex. If solvent polarity is slowly changed from nonpolar to polar, the barrier height between CIP and SSIP is reduced and free ions will be more stabilized. In a highly polar medium only free ion formation predominates. Therefore, at ϵ_{max} the potential energy barrier height would be as such where both the separation and the geminate recombination of RIPs become mostly efficient to show the maximum field effect. If value is taken into account, we could see from Figure 8 that for low values, i.e., in case of the ECZ−DCB system, this optimum barrier height is attained at much lower ϵ compared to the system where δ is quite high, e.g., in the Py−DMA system. Therefore, in ECZ−DCB ϵ_{max} would be less and field effect should start from a lower d.c. of the medium compared to that in the Py−DMA system. Further evidence for the importance of δ as a factor in determining ϵ_{max} comes from the studies with another exciplex PMC−DCB system, where another derivative of the carbazole has been used as fluorophore, keeping DCB unchanged. The alteration of ϵ_{max} value can nicely be interpreted by the same concept of extent on charge transfer. The oxidation potential (E_{ox}) of PMC is 1.0 eV, whereas that of ECZ is 1.12 eV. As E_{ox} of the donor PMC is less than that of ECZ, the extent of charge transfer enhances in PMC−DCB ($\delta = 0.7$) compared to that in ECZ−DCB ($\delta = 0.148$). The formation of CIP as well as the PE barrier height between the CIP and SSIP in PMC−DCB are enhanced compared to ECZ−DCB at a particular ϵ. Therefore ϵ_{max} in PMC−DCB ($\delta = 0.7$) should reach at higher ϵ than for ECZ−DCB ($\delta = 0.148$) and at lower but closer ϵ compared to that in Py-DMA ($\delta = 1$).[15c] Experimental observation, i.e., $\epsilon_{max} = 12$ for PMC−DCB, strongly supports the prediction.

A convenient method for evaluating the reliability of the above explanation is the comparison of the experimental findings with the results obtained from some analytical model. Here our earlier analytical model[22f,23] based on the following Smoluchowski equation

$$\Phi = \frac{1 - e^{-r_c/r_g}}{1 + (\alpha r_c/R^2 - 1)e^{-r_c/R}}$$

$$\Delta\Phi/\Phi = \text{constant} \times \frac{r_c}{1 - e^{-r_c/r_g}} \frac{(\alpha r_c/R^2 - 1)e^{-r_c/R} - e^{-r_c/r_g}}{1 + (\alpha r_c/R^2 - 1)e^{-r_c/R}}$$

where $r_c = e^2/\epsilon kT$, r_g and R = internuclear distances in SSIP and CIP, respectively, and $\alpha = 10^3/h$, where h is an adjustable parameter that estimates the potential energy difference between CIP and SSIP. It has been shown[22f] that $h = \kappa U_0/4$, where U_0 is an effective velocity of crossing the potential barrier at the reaction radius and κ is the transmission coefficient. κ is governed by the interconversion rates between CIP and SSIP. If $h = \infty$, that is, for a perfectly absorbing sink, CIPs will exist alone, which means the barrier height between CIP and SSIP is maximum. As h decreases, i.e., α increases, the barrier height between CIP and SSIP also decreases. Although the general trends of the variation, i.e., the initial rising part, maxima, etc., match well with the experimental one, this analytical model is not sufficient to produce identical curves for the entire region. In an analytical curve, $\Delta\phi/\phi$ drops more slowly with increase in ϵ in comparison to the experiment. One of the possible causes of this anomaly may be the assumption that the spin evolution rate is independent of the internuclear distance between two radical ions beyond the distance where CIP is formed. In reality, however, this may not be true. Actually spin evolution is operative only for an internuclear distance where J is negligible whereas ϕ gets contribution from the entire diffusion domain. The increase in outward diffusion process with increase in ϕ, which reduces the recombination, will then affect $\Delta\phi$ more in comparison to ϕ, causing $\Delta\phi/\phi$ to decrease faster than the analytical curve. However, despite all these drawbacks, this model is quite suitable to show the effects of δ on ϵ_{max}. In the expression the factor α, the reverse of h, determines the depth of the barrier between CIP and SSIP, and this is directly related to δ as discussed above. For best-fit lines a value is assumed to be more by 10 times in ECZ−DCB ($\alpha = 45\,000$) whereas it is slightly less in PMC−DCB ($\alpha = 5000$) when both are compared to Py−DMA ($\alpha = 4500$). These values compare qualitatively the barrier heights or the extent of CT between two exciplexes from theoretical viewpoints. Another important observation is that the R value is slightly greater in ECZ−DCB compared that in Py−DMA or PMC−DCB, which is also true in the case of complexes with fewer charge-transfer characteristics.

5. Conclusion

It is our particular interest to compare the ET reaction mechanisms in similar types of D−A pairs applying MF as a probe. It turned out that the reaction pathways strongly depend on the substitutions in A and D molecules. This understanding has been of great utility to design new systems of interest. Moreover, not only do the spin and diffusion dynamics dictate where $\epsilon_{\max}$ would appear in the mixtures of aprotic solvents for different exciplex systems, but the extent of charge separation also has a big role. The interesting and novel idea of variation in potential energy barrier between CIP and SSIP with d.c. for exciplex systems with different extent of charge separation may give a deeper insight into the mechanistic evolution of the MF theory.

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