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# An improved phase-locked detection system for the observation of the magnetic field effect on exciplex luminescence: deviation from previously observed dielectric constant dependence

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## Abstract

The magnetic field effect (MFE) on exciplex luminescence was studied using an improved phase-locked detection system. The sensitivity of the instrument gives a precise measurement of a very low percentage change in MFE (of the order of 0.01%) which has not been obtained previously. A comparative study of the dependence of MFE on the dielectric constant ($\epsilon$) of the medium was carried out using two exciplex systems: pyrene–*N,N*-dimethylaniline (Py–DMA), a well-studied exciplex system, and *N*-ethyl carbazole–1,4-dicyanobenzene (ECZ–DCB), a recently explored exciplex system. For ECZ–DCB, the MFE was obtained around $\epsilon \approx 9$ ($\epsilon_{max}$), which is far lower than the usual limit of $14 < \epsilon_{max} < 18$ observed in Py–DMA and other exciplex systems, with the onset at $\epsilon = 6$. This result was explained on the basis of the different charge transfer characteristics of the two systems. © 1997 Elsevier Science S.A.

*Keywords:* Charge transfer; Dielectric constant; *N*-Ethyl carbazole–1,4-dicyanobenzene exciplex; Magnetic field effect

## 1. Introduction

Over the past two decades, the advent of new techniques has resulted in an increased interest in the magnetic field effect (MFE) on exciplex luminescence [1–22]. This is an effective means of monitoring spin-dependent radical ion pair (RIP) recombination, a consequence of the competition between the spin evolution and spatial motion of the RIPs. In exciplex systems, the RIPs commonly originate with singlet correlation. In moderately polar medium, the partners of the solvent-caged RIPs can be separated by diffusion to a distance at which exchange interaction (J) becomes negligible. The singlet (S) and three triplet ($T_{\pm}$, $T_0$) states of the RIPs become degenerate, and the hyperfine interactions (HFIs) can cause mixing of spin conversion, which affects the singlet reaction channels, i.e. decreases the regeneration of the singlet exciplex through geminate recombination. This is, in a sense, opposite to the enhancement of the formation of the free radicals which happens in the case of the triplet yield. In the presence of an external magnetic field, when the Zeeman interaction lifts the degeneracy of the $T_+$ and $T_-$ states with the S and $T_0$ states, the situation truly resembles a two-level system. Consequently, the intersystem crossing (ISC) rate decreases significantly which, in turn, increases the geminate recombination yield and exciplex luminescence.

The diffusion dynamics of the RIPs plays a major role in the observation of the MFE. It is important to note that diffusion provides the time required for the slow spin evolution process to occur in the RIPs and thus plays a major role in the observation of the MFE. For charged RIPs, the modification of the potential energy surface by electrostatic solvent interaction is large, and can cause a change in the diffusion dynamics of the RIPs. Therefore the potential energy surfaces of RIPs should be strongly influenced by the dielectric constant ($\epsilon$) of the solvent, which has been observed previously by several workers [9–11,23–34]. Petrov et al. [11] were the first to observe the influence of $\epsilon$ on MFE of the pyrene–*N,N*-diethylaniline (Py–DEA) exciplex system in alcoholic solvent mixtures, where the effect maximizes at $\epsilon \approx 26$ ($\epsilon_{max} \approx 26$). Later, the dependence of the relative MFE ($\Delta\phi/\phi$, where $\phi$ is the exciplex luminescence intensity and $\Delta\phi$ is the enhancement of the exciplex luminescence intensity in the presence of a saturating magnetic field) on $\epsilon$ was studied for pyrene–*N,N*-dimethylaniline (Py–DMA) and 9-cyanophenanthrene–*trans*-anethole (CNP–AN) exciplex systems

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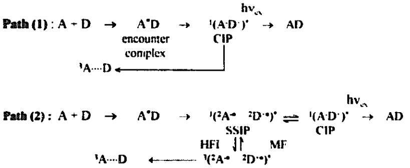
in both alcoholic and non-alcoholic solvent mixtures [23–31]. In alcoholic solvents, Py–DMA and CNP–AN systems exhibit $\epsilon_{max} = 28$ and $\epsilon_{max} = 40$ respectively, but in non-alcoholic solvent mixtures both systems show $\epsilon_{max}$ within the limit $14 < \epsilon < 18$ after the onset of $\Delta\phi/\phi$ at $\epsilon \approx 9$. The influence of $\epsilon$ on the MFE can be clearly understood qualitatively from the potential energy diagrams, which have been described in detail previously [23,26–29,32,34,35]. It has been suggested that, towards lower $\epsilon$, the potential energy curve is such that a larger fraction of molecules undergo charge transfer (CT). Therefore direct exciplex formation is highly favourable without MFE (path 1) [23,34]. It is insignificant at higher $\epsilon$ where free radical formation from RIPs predominates. Only in moderately polar media, with intermediate $\epsilon$, are most of the RIPs involved in diffusion, spin evolution and geminate recombination, which are influenced by an external magnetic field (path 2) [23,34].



CIP and SSIP stand for contact ion pair and solvent-shared ion pair respectively. Both are geminate RIPs encapsulated in a solvent cage: in CIP, the two ions are in contact with each other; in SSIP, the two ions are separated by intermediate solvent molecules. Therefore a potential energy barrier exists between SSIP and CIP, which represents the energy required to squeeze out the intermediate solvent molecules [23,34].

Why MFE maximizes within the above limit of $\epsilon$ in different non-alcoholic mixtures and whether this is true irrespective of the exciplex system used remain a matter of controversy. These questions cannot be regarded as resolved due to the lack of extensive studies with different types of exciplex system.

The purpose of this study is to investigate whether the influence of $\epsilon$ on the MFE in aprotic solvents remains unchanged irrespective of the exciplex system used; a highly sensitive detection system was employed.

## 2. Experimental details

An improved version of the phase-locked detection system used in earlier work [16,17] was employed here to study the dependence of the steady state singlet luminescence on the magnetic field. This home-built apparatus uses full-wave, phase-sensitive detection (PSD) in lieu of half-wave PSD as employed in earlier work [18]. The magnet with the sample cuvette between the poles was placed inside a commercial nanosecond laser flash photolysis chamber (Applied Photophysics), and the sample was excited transversely by the UV light (using IR and visible cut-off filters (Oriel 52190) and collimating optics) from a current-stabilized 250 W xenon lamp. The luminescence was collected through a small hole in one pole of the magnet by the conventional double lens optics and monochromator of the chamber and was detected by a 1P28 photomultiplier biased for low-current, high-gain operation with a load impedance of 1 MΩ. The reduction of shot noise and the use of a stabilized Xe lamp with full-wave lock-in and better optical coupling effectively lead to a high signal-to-noise (S/N) ratio, and the luminescence change can be detected to an accuracy of better than 1 part in 10 000 (Fig. 1). The electronics were tested for linearity, long-term stability and the lack of spurious effects using pyrene excimer luminescence.

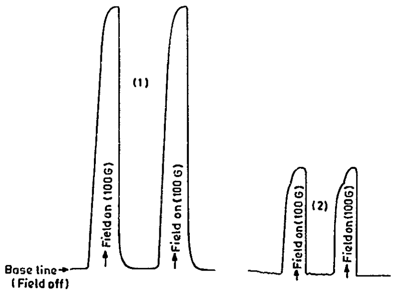


Fig. 1. Signals for MFE on exciplex luminescence of Py($10^{-4}$ M)–DMA($6.2\times10^{-2}$ M) in THF–DMF at $\epsilon = 14$, $\phi = 27$ mV, $\Delta\phi = 2.46$ mV and $\Delta\phi/\phi = 9\%$ (1) and ECZ($5\times10^{-4}$ M)–DCB($4\times10^{-2}$ M) in THF–DMF at $\epsilon = 9$, $\phi = 27$ mV, $\Delta\phi = 0.37$ mV and $\Delta\phi/\phi = 1.37\%$ (2). $\phi$ is the photomultiplier signal in millivolts signifying the relative exciplex luminescence intensity. Two similar peaks for each exciplex show the experimental accuracy and reproducibility.

Py, DMA, *N*-ethyl carbazole (ECZ) and 1,4-dicyanobenzene (DCB) were obtained from Aldrich (99% purity). Only DMA was purified by vacuum distillation, and the other compounds were used without further processing. Spectroscopic grade tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), benzene (Bz) and acetonitrile (MeCN) were used after appropriate distillation. The working solutions were prepared with fixed donor and acceptor concentrations of [Py] : [DMA] = $10^{-4}$ M : $6\times10^{-2}$ M for the Py–DMA exciplex system and [ECZ] : [DCB] = $5\times10^{-4}$ M : $4\times10^{-2}$ M for the ECZ–DCB exciplex system. All the samples were deoxygenated by bubbling pure, dry Ar gas for 40 min and were used within 1 h after preparation. Several checks were made during the experiments for possible degradation of the sample.

## 3. Results and discussion

Figs. 2(a) and 2(b) show the $\Delta\phi/\phi$ vs. $\epsilon$ and $\phi$ vs. $\epsilon$ curves respectively at saturating magnetic field for Py–DMA

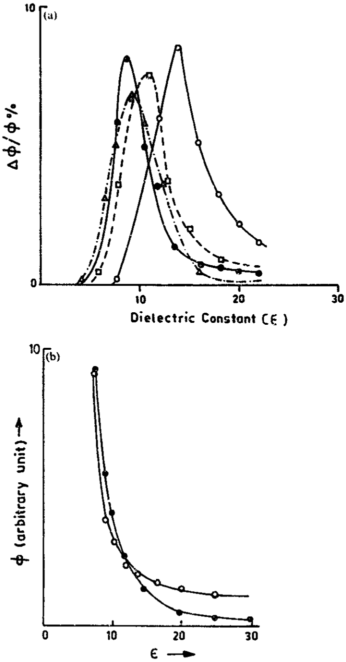


Fig. 2. (a) $\Delta\phi/\phi$ vs. $\epsilon$ curves at saturating magnetic field for Py($10^{-4}$ M)–DMA($6.2\times10^{-2}$ M) (○) and ECZ($5\times10^{-4}$ M)–DCB($4\times10^{-2}$ M) (●) in THF–DMF. The dotted and broken lines represent $\Delta\phi/\phi$ vs. $\epsilon$ for ECZ–DCB in Bz–DMF (△) and Bz–MeCN (□) respectively. (b) $\phi$ vs. $\epsilon$ curves at saturating magnetic field for Py($10^{-4}$ M)–DMA($6.2\times10^{-2}$ M) (●) and ECZ($5\times10^{-4}$ M)–DCB($4\times10^{-2}$ M) (○) in THF–DMF. The curves for ECZ-DCB are fivefold magnified to compare with the curve of Py-DMA.

in THF–DMF and ECZ–DCB [34] in THF–DMF, Bz–MeCN and Bz–DMF. The instrument is so sensitive that increases in $\Delta\phi/\phi$ were observed at $\epsilon\approx6$ (not identified in earlier experiments) [23-31]. A dramatic difference can be seen when comparing Py–DMA and ECZ–DCB systems: in the latter system, $\epsilon_{max}\approx9$, i.e. far lower than the usual limit $14<\epsilon<18$ (Fig. 2(a)). This shows that the earlier result regarding the maximum effect of $\epsilon$ on MFE in aprotic solvents is not applicable for all types of exciplex system.

Previously, we have shown in detail that a marked difference exists between the characteristics of Py–DMA and ECZ–DCB exciplex systems [34]. The difference between the oxidation and reduction potentials of Py ($E^{ox}_{Py}=0.78$ eV) and DMA ($E^{red}_{DMA}=-2.10$ eV) is larger than that between ECZ ($E^{ox}_{ECZ}=1.10$ eV) and DCB ($E^{red}_{DCB}=-1.65$ eV) by 0.13 eV. This is reflected in the extent of charge separation between the partners of these two exciplex systems. Following the Lippert–Mataga equation, it has been shown that the extent of CT ($\delta$) in ECZ–DCB is almost one-eighth of that in Py–DMA, where almost complete CT takes place, i.e. $\delta$ is assumed to be equal to unity [34]. This indicates that ECZ–DCB is a typical heteroexcimer, whereas Py–DMA is a typical exciplex. The smaller CT character in ECZ–DCB favours the formation of a weak exciplex even in solvents of high $\epsilon$ (e.g. MeCN), which is improbable in Py–DMA as shown in Fig. 2(b). Therefore it is quite logical to assume that the diffusion dynamics of the partners of the RIPs in the ECZ–DCB system will be very different from the diffusion dynamics of the partners of the RIPs in the Py–DMA system; this should be visualized in a marked difference in the dependence of MFE on $\epsilon$ of the medium, an interplay of the spin and diffusion dynamics of RIPs, between these two systems.

To verify the above statement, the simple analytical formalism based on Smoluchowski's diffusion equation [27–29,36,37], later used [29,36,37] to explain successfully the solvent polarity dependence of MFE in Py–DMA and CNP–AN systems, has been considered here. Assuming that spin motion and spatial motion are independent, and using the semi-classical numerical results of Schulten et al. for the spin evolution dynamics and Hong and Noolandi's exact analytical solution of Smoluchowski's equation with coulombic field for the spatial dynamics, the following expressions were deduced

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

and

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

where $r_c=e^2/\epsilon kT$, $r_g$ and $R$ are the internuclear distances in SSIP and CIP respectively, $\alpha=10^3/h$ and $h$ is an adjustable parameter which estimates the potential energy difference between CIP and SSIP [27–29,36,37].

Fig. 3 shows that the theoretical best fit with the experimental data of the ECZ–DCB system can be achieved only if the value of $\alpha$ is enhanced tenfold compared with that of the Py–DMA system, keeping the other variables $r_g$ and $R$ almost the same. The increase in $\alpha$ implies a decrease in the $h$ value, which signifies the reduced potential energy barrier between CIP and SSIP in ECZ–DCB compared with that in Py–DMA [23,34]. In moderately polar aprotic solvent mixtures, the potential energy difference between CIP and SSIP is determined mainly by the extent of CT between the partners of the RIPs. The smaller the CT, the smaller the activation barrier between CIP and SSIP, i.e. less energy will be required to squeeze out the solvent molecules trapped between the partners of the RIPs for the conversion of SSIP to CIP in ECZ–DCB compared with that in Py–DMA [23,34]. This may be further correlated with the observations reported previously from triplet state studies using laser flash photolysis that, even in polar medium (MeCN), the ECZ–DCB exciplex is formed following both pathways (1) and

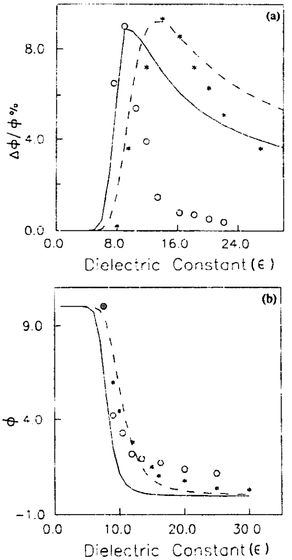


Fig. 3. Comparison of the theoretical $\Delta\phi/\phi$ vs. $\epsilon$ (a) and $\phi$ vs. $\epsilon$ (b) curves for ECZ–DCB (full line) and Py–DMA (broken line) with the experimental data points (O and * respectively) in THF–DMF. Parameter values for the theoretical curves: $\alpha = 45\,000$, $r_g = 8$ Å and $R = 7$ Å for ECZ–DCB and $\alpha = 4500$, $r_g = 8$ Å and $R = 6$ Å for Py–DMA.

(2), i.e. direct formation of CIP and indirect formation of CIP through SSIP respectively, whereas in Py–DMA only path (2) occurs [34]. This indicates that a sharp line of demarcation does not exist in the energy change between CIP and SSIP in the ECZ–DCB system, in contrast with Py–DMA where a distinct energy barrier exists between the two [23]. More specifically, due to the existence of this energy barrier in Py–DMA, a moderately higher dielectric medium is required, compared with that for ECZ–DCB, to maximize the SSIP ↔ CIP conversion experiencing the highest MFE during the spatial motion of the partners of the RIPs. Therefore it can be concluded that the lower CT character, the manifestation of which is the lower energy barrier between CIP and SSIP in ECZ–DCB, is mainly responsible for shifting $\epsilon_{max}$ to a lower value compared with that in Py–DMA.

The initial rising part of the $\Delta\phi/\phi$ vs. $\epsilon$ curve of ECZ–DCB fits well with the experimental curve (Fig. 3(a)). However, with an increase in $\epsilon$, the theoretical $\Delta\phi/\phi$ value decreases much more slowly than the experimental data points. This is probably due to the discrepancies which exist between the theoretical and experimental $\phi$ vs. $\epsilon$ results as shown in Fig. 3(b). MFE on exciplex luminescence can be observed when an equilibrium exists between SSIP and CIP and SSIP and free ions as in path (2). Therefore path (1) is independent of the magnetic field. In formulating the analytical model, it has been considered that the actual value of $\phi$ in $\Delta\phi/\phi$ should only be due to CIPs in equilibrium with SSIPs as in path (2). However, in ECZ–DCB, the experimental $\phi$ value is the summation of the luminescence of CIPs generated following both pathways, one of which is independent of the magnetic field. Therefore, in ECZ–DCB, the experimental $\phi$ values are always greater than the theoretical $\phi$ values, which does not occur in Py–DMA where only path (2) exists (Fig. 3(b)); a rapid fall-off in the experimental $\Delta\phi/\phi$ values with $\epsilon$ compared with the theoretical values is observed in ECZ–DCB. Further experimental and analytical studies are being performed and will be reported later.

## 4. Conclusions

The unique feature of this work lies in the observation that the polarity of the medium does not have sole control over the maximum MFE; the nature and extent of CT of the exciplex system also play a major role. This observation is a very important step towards the elucidation of the overall mechanism. The MFE of different types of exciplex system will provide a better understanding of the process.

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