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Dielectric Dependence of Magnetic Field Effect: A Tool for Identification of Exciplex and Triplex[‡]

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The molecule, 4,4′-bis(dimethylamino)diphenylmethane (DMDPM), having two potential donor sites is able to form both luminescent exciplex (1:1) and triplex (1:2) with photoexcited pyrene (PY), which is inferred from the maximization of magnetic field effects at two different dielectric constants of the solvent media. The DMDPM molecule can be considered as two *N*,*N*-dimethylaniline (DMA) molecules linked through a methylene chain. Therefore, electron hopping is likely to occur from one DMA unit to the other through the intermediate $>CH_2$ group, which is reflected in the $B_{1/2}$ measurements and is in agreement with Schulten's theory of intramolecular electron exchange. The nature of charge transfer and electron hopping is substantiated with theoretical calculations highlighting relative orientations of PY and DMDPM.

1. Introduction

An external low magnetic field (MF) can be used as a tool to identify the original spin states of the radical ion pairs (RIPs) formed through photoinduced electron transfer (PET) reactions. The inherent electron spin—a nuclear spin coupled hyperfine interaction (HFI) of the system—induces intersystem crossing between singlet (S) and three-degenerate-triplet (T_0, $T_\pm$) states. When the external MF overcomes this HFI, $S \rightarrow T_\pm$ transitions are totally blocked because of nondegeneracy among the triplet states. This nondegeneracy is a consequence of Zeeman splitting. Thus, MF enhances the singlet product (exciplex[1,8]) when the RIPs are initially formed in a singlet state whereas the triplet product (free ions) is enhanced when the RIPs are initially in a triplet state.

Similar studies involving simple donor (D) and acceptor (A),[6,7] linked D−A,[3,4] and models mimicking biological systems[9] showing the above-mentioned properties have been studied thoroughly during the last three decades. The current communication presents a photophysical study of PET reaction between A and D, namely, pyrene (PY) and 4,4′-bis(dimethylamino)diphenylmethane (DMDPM), respectively. The novelty of the DMDPM molecule (Figure 1) lies in its structure where two *N*,*N*-dimethylaniline (DMA) units are linked through a $>CH_2$ group. This makes DMDPM a molecule with two potential donor sites. To complete the study, we have compared the present PY-DMDPM system with the earlier reported PY-DMA system containing only one donor site.[6] In our PY-DMDPM system, in addition to the normal 1:1 complex (exciplex), we also observed a unique 2:1 complex (triplex). The dependence of a magnetic field effect (MFE) on solvent dielectric constant (ϵ) was used to identify the triplex and the exciplex.

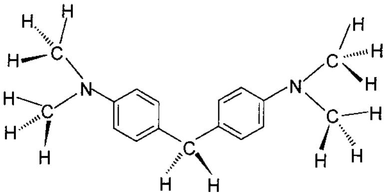

Figure 1. Structural formula of 4,4′-bis(dimethylamino)diphenylmethane (DMDPM).

Any variation in the width of RIP-spin sublevels is reflected in the value of $B_{1/2}$ (the field strength at which MFE reaches half of its saturation value). Moreover, both experimental[6f,8a,b] and theoretical[10] studies have established that the width of these sublevels is influenced by the electron hopping or exchange process between the cation radical of the electron donor and its diamagnetic counterpart,

$$D^{\bullet+} + D \leftrightarrows D + D^{\bullet+}$$

The rate of electron hopping increases with increases in D concentration. For example, $B_{1/2}$ for PY-DMA is 6.2 millitesla (mT) at 2×10^{-2} M DMA concentration and it subsequently increases to 7.0 mT[6f] at a DMA concentration of 6×10^{-2} M. However, an increase in D concentration also affects other physical parameters of the system e.g., polarity, viscosity etc. Even a slight alteration in these parameters may indirectly influence the measurement of MFE. A better alternative to increase the D concentration is to link the D molecules by methylene chain. The shorter the chain length, the higher is the rate of electron exchange.[11] The electron exchange in the DMDPM molecule on electron transfer (ET) can be represented as

$$DMA-CH_2-DMA^{\bullet+} \leftrightarrows DMA^{\bullet+}-CH_2-DMA$$

or simply

$$D-CH_2-D^{\bullet+} \leftrightarrows D^{\bullet+}-CH_2-D$$

[‡] Abbreviations: MF, magnetic field; RIP, radical ion pair; PET, photoinduced electron transfer; HFI, hyperfine interaction; D, donor; A, acceptor; PY, pyrene; DMDPM, 4,4′-bis(dimethylamino)diphenylmethane; DMA, *N*,*N*-dimethylaniline; MFE, magnetic field effect; mT, milli Tesla; ET, electron transfer; THF, tetrahydrofuran; DMF, *N*,*N*-dimethylformamide; Q, quencher.

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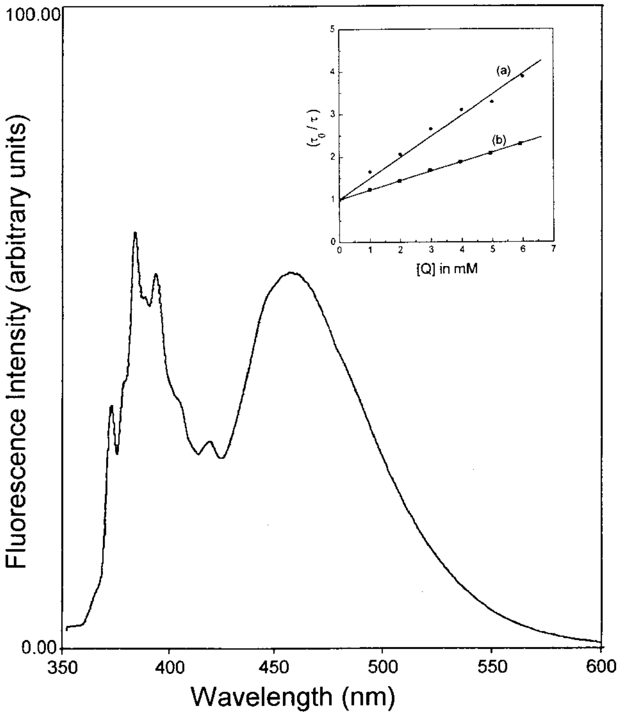


Figure 2. Fluorescence emission spectrum of PY (1×10^{-4} M) in the presence of DMDPM (4×10^{-3} M) in cyclohexane showing exciplex peak around 460 nm. Excitation wavelength is 337 nm, which is characteristic of PY. Inset: Lifetime quenching plots of (a) PY-DMDPM and (b) PY-DMA using varying concentration of quencher [Q] in acetonitrile. Concentration of PY used is 1×10^{-4} M.

Here we have made an attempt to study the intramolecular electron exchange phenomenon in both the exciplex and the triplex formed between PY and DMDPM.

2. Experimental Section

Materials. Pyrene (PY), purchased from Aldrich, was used without any further purification. The donor, DMDPM, was bought from Merck and was crystallized from 70% ethanol and air-dried. The other donor, DMA (BDH), was used after proper distillation. Spectragrade cyclohexane, tetrahydrofuran (THF, $\epsilon = 7.58$), *N,N*-dimethylformamide (DMF, $\epsilon = 36.7$), acetonitrile, ethanol (EtOH, $\epsilon = 24.3$), and methanol (MeOH, $\epsilon = 33.0$) were used as solvents without further purification. The solutions were deoxygenated whenever required by passing through dry argon gas.

Apparatus. Absorption and fluorescence spectra were recorded by Shimadzu UV-2101 PC spectrophotometer and a Hitachi spectrophotometer (model 4010), respectively. Fluorescence lifetimes were measured by a time-correlated-single-photon counting spectrophotometer (Edinburgh) with a lamp having full width at half-maximum of 1.2 ns and repetition rate of 25 kHz. The increase in exciplex luminescence ($\Delta\phi$, where ϕ is the luminescence in absence of MF) was studied using a full-wave phase-sensitive detection system described elsewhere.[7d,e] The signal-to-noise ratio of this system is 1000:1 and it is sensitive enough to detect a 0.1% change in $\Delta\phi/\phi$ %, a measure of MFE.[7a]

3. Results

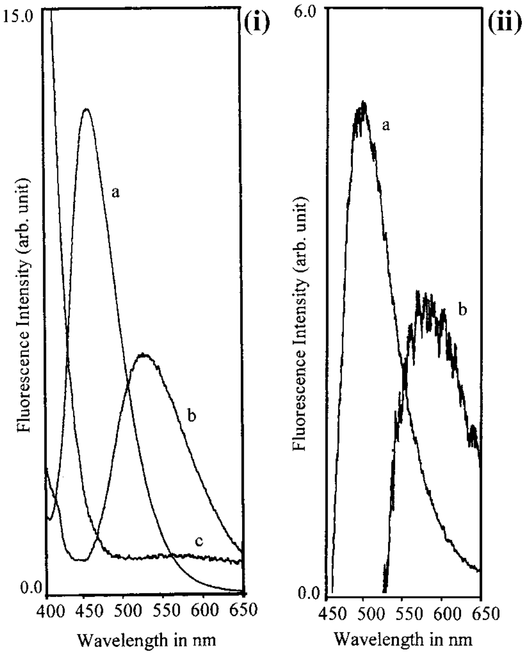


Figure 3. Fluorescence spectra of (i) exciplex with 1×10^{-4} M PY and 2×10^{-2} M DMDPM in (a) cyclohexane, (b) tetrahydrofuran, and (c) acetonitrile (ii) triplex with 5×10^{-4} M PY and 2×10^{-2} M DMDPM in (a) cyclohexane and (b) tetrahydrofuran obtained by subtraction[7a] method. Excitation wavelength is 337 nm, which is characteristic of PY.

(a) Fluorescence Measurements. Figure 2 shows fluorescence emission spectra of the PY monomer and PY-DMDPM exciplex. The inset of Figure 2 depicts the plot of fluorescence lifetime (τ) quenching (for PY-DMDPM and PY-DMA systems) at varying concentrations of quencher (Q; DMDPM and DMA) in acetonitrile. The bimolecular quenching constant, k_q, is given by the equation,[7h]

$$\tau_0/\tau = 1 + k_q\tau_0[Q] \qquad (1)$$

where τ_0 is the lifetime of the fluorophore in the absence of Q. The calculated k_q values are $33.9 \pm 1.8 \times 10^9$ (mol dm^{-3} s^{-1}) for PY-DMDPM and $15.1 \pm 1.0 \times 10^9$ (mol dm^{-3} s^{-1}) for PY-DMA systems in acetonitrile solution. These values indicate complete dynamic quenching. The k_q value of PY-DMDPM is twice that of PY-DMA, presumably resulting from the presence of two donor sites in DMDPM.

(b) Study of MFE on Exciplex Luminescence. Initially we measured MFE on the PY-DMDPM system at 520 nm (a λ close to the exciplex peak) in aprotic THF-DMF solvent mixtures of varying ϵ using saturating MF of 0.014 T. Two maxima at $\epsilon \sim 13$ and $\epsilon \sim 15$ were obtained in the plot of $\Delta\phi/\phi$ % versus ϵ. This clearly indicates the possibility of formation of two types of complexes involving the same D−A pair. It is to be noted that the PY-DMA system shows a single maximum in both THF-DMF and EtOH-MeOH solvent mixtures at $\epsilon \sim 14$[6b] and $\epsilon \sim 29$,[6f] respectively.

The steady-state fluorescence shows the emergence of an additional peak in both cyclohexane and THF solvents with variation in the concentration of PY (Figure 3). Quenching of fluorescence intensity, as well as lifetime with gradual increases in PY concentration (Table 1) in cyclohexane, indicate formation of the triplex from the exciplex, that is, PY-DMDPM...PY. To characterize the above process, variation of $\Delta\phi/\phi$ % with ϵ was carefully studied again in THF-DMF using different PY concentrations and monitoring at two λ values (520 and 590 nm). Table 2 gives the values of the maximum $\Delta\phi/\phi$ % at two ϵ values at each of the two wavelengths with different PY concentrations. Figure 4 demonstrates the change in $\Delta\phi/\phi$ % with increasing ϵ at two λ values, 520 and 590 nm.

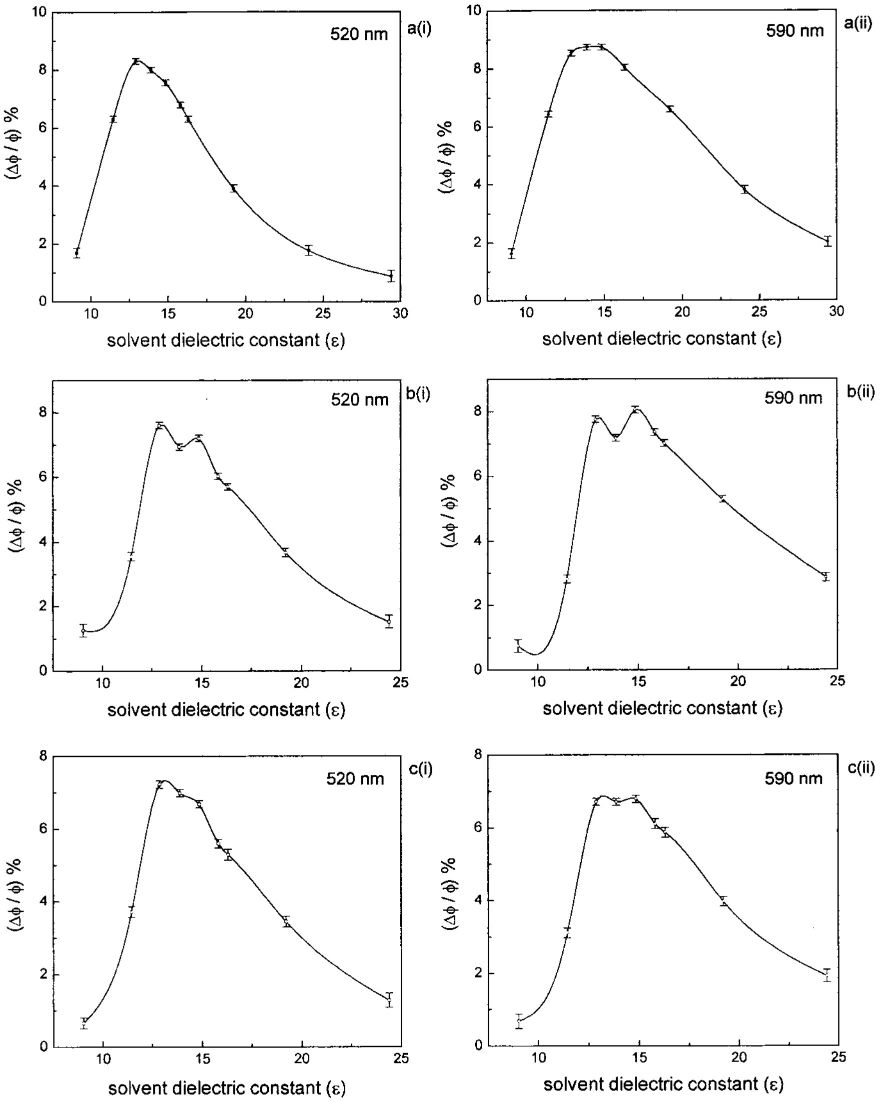


Figure 4. Variation of **$\Delta\phi/\phi$** % with ϵ for PY-DMDPM at different PY concentrations (a) 5×10^{-4} M PY, (b) 1×10^{-4} M PY, (c) 5×10^{-5} M PY in THF-DMF mixtures. The measurements were done at (i) 520 nm and (ii) 590 nm under saturating MF of 0.014 T and a DMDPM concentration of 2×10^{-2} M.

TABLE 1: Variation of Fluorescence Intensities and Lifetimes of PY-DMDPM Exciplex and Triplex with Varying Concentration of PY[a]

		lifetime measurements (ns)	
concentration of PY (M)	fluorescence intensity (arbitrary unit) at 460.8 nm	PY-DMDPM exciplex at 460 nm	PY-DMDPM triplex at 510 nm
5×10^{-5}	83.32	49.61 ± 0.1	
1×10^{-4}	61.15	28.94 ± 0.2	23.76 ± 0.2
5×10^{-4}	12.73	24.24 ± 0.2	21.88 ± 0.2

[a] The concentration of DMDPM was 2×10^{-2} M in all the sets.

TABLE 2: $\Delta\phi/\phi$ % at Two Different ϵ Values Measured at Two λ Values for PY-DMDPM System in THF-DMF and EtOH-MeOH Mixtures

concentration of PY (M)	solvent mixture	ϵ	λ_1, nm	$\Delta\phi/\phi$ %	λ_2, nm	$\Delta\phi/\phi$ %
5×10^{-4}	THF-DMF	~13	520	8.3 ± 0.1	590	8.5 ± 0.1
		~15		7.6 ± 0.1		8.7 ± 0.1
1×10^{-4}	THF-DMF	~13	520	7.6 ± 0.1	590	7.8 ± 0.1
		~15		7.2 ± 0.1		8.0 ± 0.1
5×10^{-5}	THF-DMF	~13	520	7.2 ± 0.1	590	6.7 ± 0.1
		~15		6.8 ± 0.1		6.8 ± 0.1
5×10^{-4}	EtOH-MeOH	~28.0	540	0.71 ± 0.1	600	0.74 ± 0.1
		33.0[a]		0.57 ± 0.1		0.90 ± 0.1

[a] Since alcohols with ϵ higher than 33 were not available we could not point out precisely the exact ϵ_{max} for PY-DMDPM at 600 nm in EtOH-MeOH mixture.

In the second set of experiments, we studied MFE on a PY-DMDPM system in a protic alcoholic (EtOH-MeOH) mixture with varying ϵ. Figure 5 depicts the effect of application of 0.014T MF on PY-DMDPM at two λ values; 540 and 600 nm (exciplexes undergo red shifting on increasing ϵ). The values are given in Table 2.

4. Discussion

(a) MFE on Exciplex Luminescence. As discussed earlier, MFE on exciplex luminescence is a diffusion-controlled phenomenon, and therefore, solvent polarity plays a major role. Earlier studies on different systems such as PY-DMA,[6b,f] 9-cyanophenanthrene-trans-anethole,[6d] and linked PY$-$(CH$_2$)$_n$$-$DMA[4a] etc. confirmed the need for moderate ϵ for maximization of MFE, except for a linked Phenanthrene-(CH$_2$)$_n$-DMA system where a continuous increase was observed.[3b,c]

The variation of MFE with the change in the concentration of PY indicates that there is a high probability of existence of a complex with two acceptors and a donor, i.e., triplex. This is

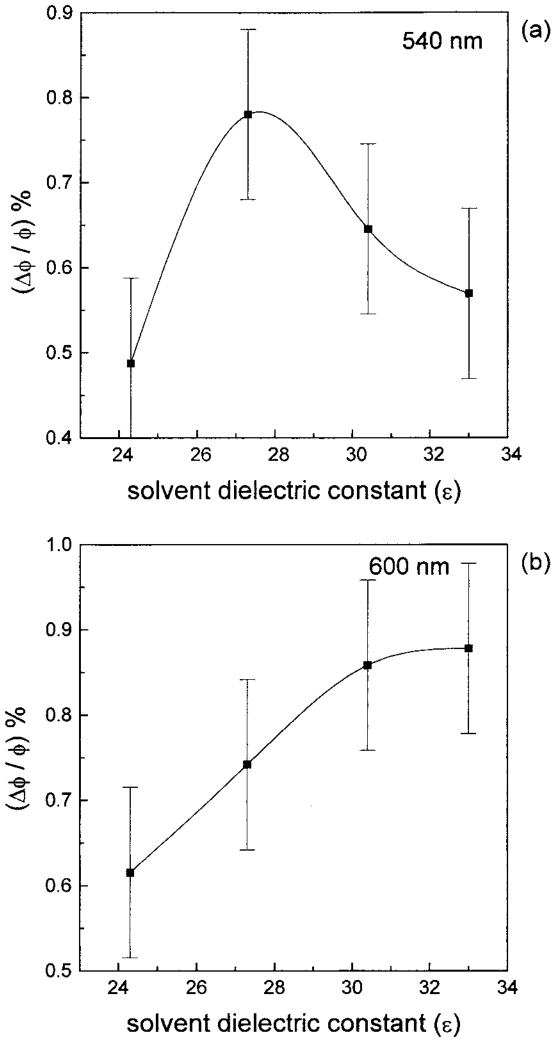
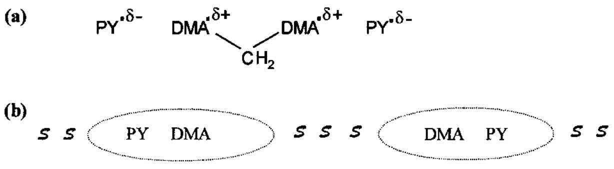


Figure 5. Variation of $\Delta\phi/\phi$ % with ϵ for PY-DMDPM in EtOH-MeOH mixtures under a saturating MF of 0.014 T with 5×10^{-4} M PY and 2×10^{-2} M DMDPM, measured at two wavelengths, (a) 540 nm and (b) 600 nm.

SCHEME 1



s represents a solvent molecule

also clear from Table 2 and the discussion in section 3 (b). Therefore, it can be intuitively hypothesized that the complex emitting at higher wavelength is a triplex with two PY molecules and a DMDPM molecule, i.e., PY:DMDPM:PY, and the one emitting at lower wavelength is an exciplex, i.e., PY:DMDPM. On the other hand, the molecule DMA with one donor site can only form an exciplex (PY:DMA), which shows $\epsilon_{\mathrm{max.}} \sim 14$[6b] in the same solvent mixture.

(b) Measurement of $B_{1/2}$. The $B_{1/2}$ value can be obtained analytically using the relation proposed by Weller et al.[8]

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

where B_1 and B_2 are the effective HFI of the D and A, respectively. $B_{1/2}$ is experimentally estimated from the plot of $\Delta\phi$ vs B (Figure 6).

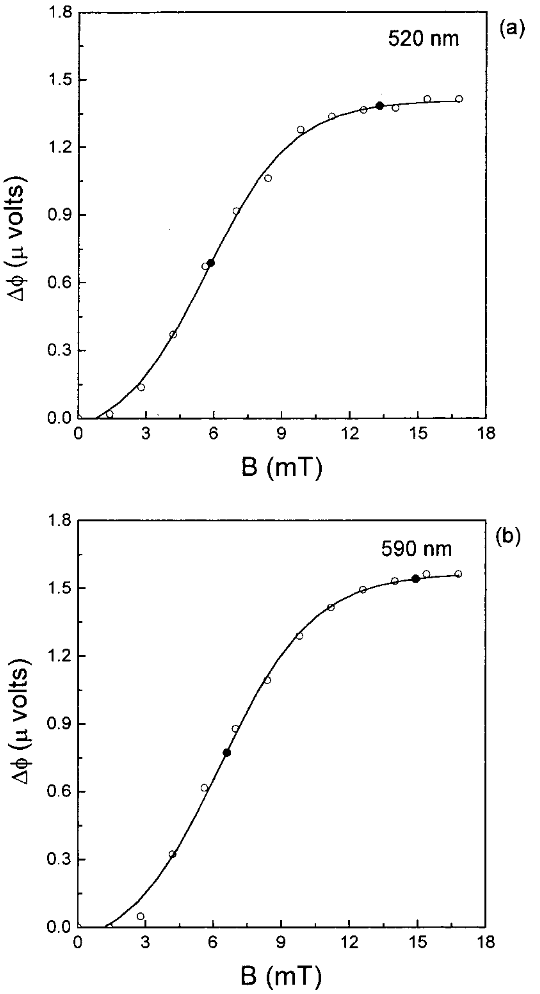
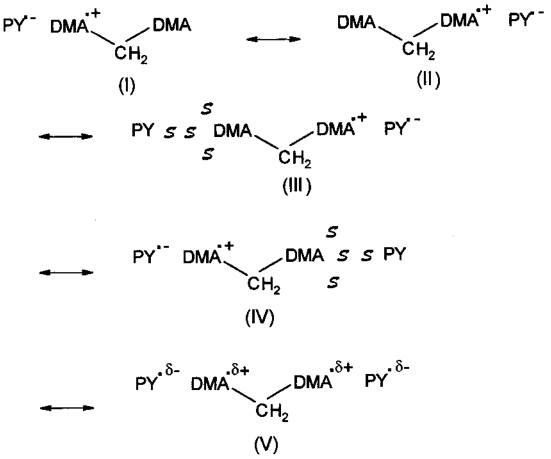


Figure 6. Plot of $\Delta\phi$ vs B (applied MF in mT) using 5×10^{-4} M PY and 2×10^{-2} M DMDPM in THF-DMF mixture, at (a) 520 nm ($B_{1/2} = 5.87 \pm 0.01$ mT) and (b) 590 nm ($B_{1/2} = 6.62 \pm 0.01$ mT). (● → representing the saturation and half saturation points in each graph.)

SCHEME 2



The PY-DMDPM system at 590 nm, where triplex formation predominates, can be depicted as shown in Scheme 1 (a) and the overall system can be considered as two nearby PY-DMA systems in solution (Scheme 1(b)). This can happen only in a freely diffusing system with high D concentration. The overall effect is an increase in the $B_{1/2}$ value. We do observe an increase in the $B_{1/2}$ value (6.62 mT) though the change is not as large as expected for free system. Since the DMDPM molecule is a methylene-linked DMA system, there is always a possibility of

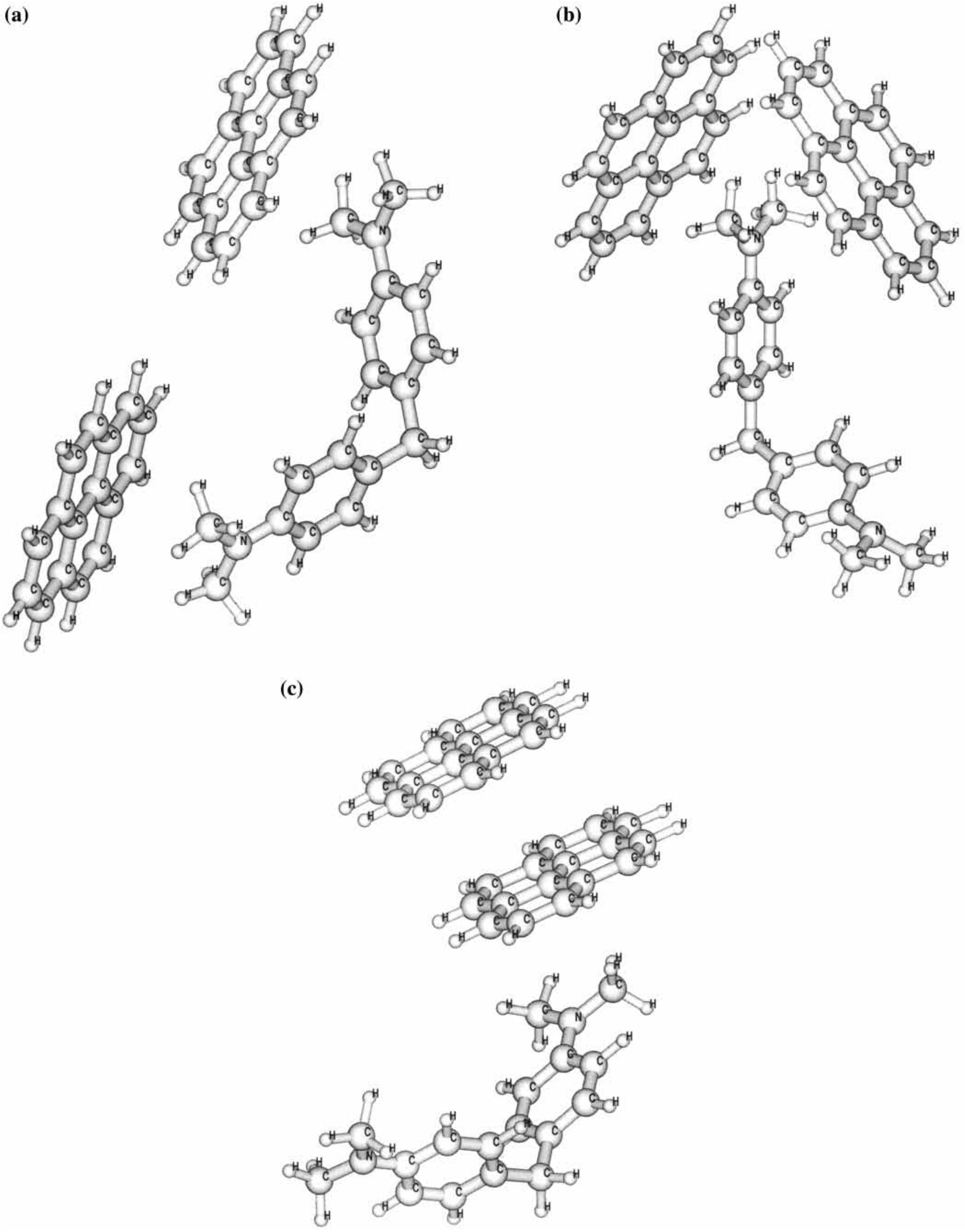


Figure 7. Geometrically optimized structures of three possible orientations of 2:1 complex of PY-DMDPM. (a) Orientation-1, (b) Orientation-2 and (c) Orientation-3. Orientation-3 has not been considered for further calculations because of its unfavorable potential energy (See text for details). The conformations of PY-DMA and 1:1 complex of PY-DMDPM are similar to (a) in regard of equivalent spatial orientation of PY with respect to DMA/DMDPM.

TABLE 3: Energies and Mulliken Charges of the Different Complexes in Both Ground and Excited States

complexes	PY-DMA	PY-DMDPM (1:1)	PY-DMDPM (2:1) orientation-1	PY-DMDPM (2:1) orientation-2
ground-state energy (hartree)[a]	−970.1078	−1369.5374	−1977.8868	−1977.8837
excited-state energy (hartree)	−969.9237	−1369.3598	−1977.7150	−1977.7132
ΔE (kcal/mol)[b]	115.52	111.45	107.81	106.99
ground-state charges	PY: 0.0054 D: −0.3588[c]	PY: 0.0083 D1: −0.3546[d] D2: −0.3068	PY1: 0.0091 PY2: 0.0089 D1: −0.3594 D2: −0.3600	PY1: 0.0062 PY2: 0.0067 D1: −0.3516 D2: −0.3231
excited-state charges	PY: −0.9871 D: 0.1803	PY: −0.9819 D1: 0.2203 D2: −0.2824	PY1: −0.9791 PY2: 0.0087 D1: 0.2133 D2: −0.3313	PY1: 0.0077 PY2: −0.9850 D1: 0.2233 D2: −0.3013

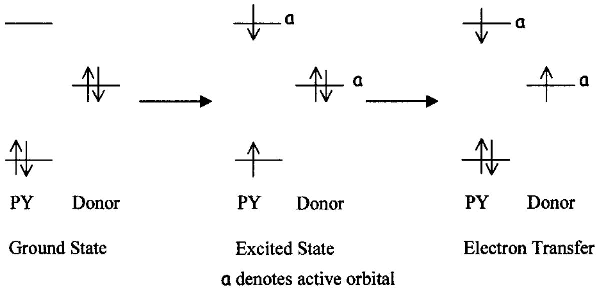
[a] Ground-state energy of orientation-3 is −1977.8045 hartree. [b] $\Delta E = [E_{\mathrm{ex}}\,(\text{complex}) - E_{\mathrm{gr}}\,(\text{complex})] \times$ unit conversion factor (627.51). [c] D represents donor site, i.e., $-\mathrm{N(CH_3)_2}$ moiety of DMA or DMDPM. [d] D1 and D2 represent the first and second donor sites of DMDPM, respectively.

"through bond electron exchange". According to Schulten's theory,[10a] this should lower the $B_{1/2}$ value. The competition between the two opposing factors: (i) increase in DMA concentration and (ii) electron exchange, results in a net increase in the $B_{1/2}$ value which is small but distinct. The intramolecular-electron-hopping process becomes much more prominent when $B_{1/2}$ is measured at 520 nm, where exciplex predominates. As our experiments were carried out at steady state, the results obtained are averaged over a time scale. Hence, one should consider a number of possible orientations of PY and DMDPM with respect to each other in solution, produced by the electron-hopping process (Scheme 2). Among these the structures, III, IV, and V resemble the triplex. These triplexes may considerably increase the time-averaged $B_{1/2}$ value. According to Schulten's theory, the $B_{1/2}$ value for the linked PY-DMA$_2$ system[10a] was predicted to change from 6.1 mT to 4.5 mT. Since in our system it is impossible to isolate the exciplex from the triplex, a similar change in the $B_{1/2}$ value could not be observed. However, the decrease in the $B_{1/2}$ value (5.87 mT) for the same system, when measured at 520 nm, does focus on the presence of an electron exchange in the DMDPM molecule following Schulten's theory.[12] In the case of PY-DMA at 2×10^{-2} M DMA concentration, the $B_{1/2}$ measured was 6.2 mT.[6f]

We have made a prior prediction of the formation of two types of complexes, exciplex and triplex. However, after becoming familiar with electron exchange, a closer study of Figure 4 is required. Since MFE on exciplex luminescence is a combination of spin evolution, diffusion dynamics, and geminate recombination of RIPs, a frequent crossover among all the structures given in Scheme 2 will prevail. Therefore, both a 1:1 complex and a 2:1 complex may coexist in solution (apparent from Figure 4). In the plots of $\Delta\phi/\phi$ % versus ϵ measured at 520 nm (4a(i), 4b(i) and 4c(i)), the fractional contribution of exciplex is greater, while for the other three plots (4a(ii), 4b(ii) and 4c(ii)) measured at 590 nm, the triplex contribution is greater.

The observations differ in protic-solvent mixtures such as alcoholic mixtures (EtOH-MeOH). A unique caging effect of the −OH groups[6b,g] adds an additional barrier for diffusion of the contact ion pair and the solvent-separated ion pair.[7] Hence, a larger ϵ is required to maximize the MFE. In the case of the PY-DMA system, the MFE maximizes at $\epsilon \sim 29$[6f] in an EtOH-MeOH mixture, which was earlier observed at $\epsilon \sim 14$ in the THF-DMF mixture. Considering this effect in the PY-DMDPM system, it is quite apparent that the triplex will be more stabilized resulting from an overall increase in the caging effect. As the triplex remains trapped in the solvent cage, a larger ϵ is required for separating it from the exciplex. It is evident from Figure 5 that at 540 nm MFE maximizes at $\epsilon \sim 28$, whereas, at 600 nm we observe a continuous increase in $\Delta\phi/\phi$ %, followed by a saturation at $\epsilon \sim 33$.

SCHEME 3



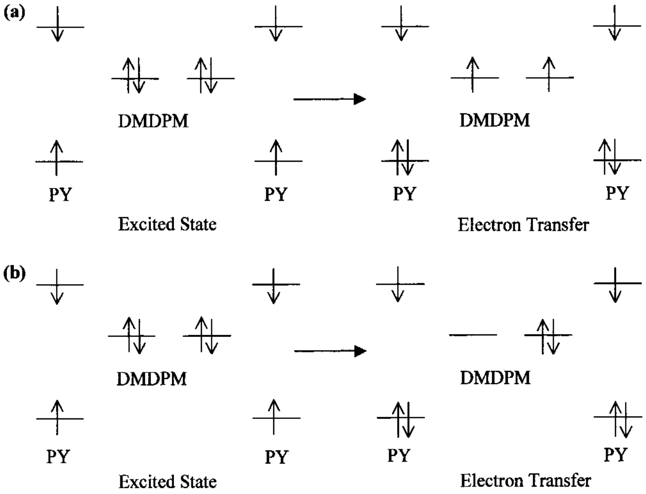
5. Theoretical Aspect

With the aim of characterizing the structures of the excited-state complexes and the nature of the ET process, we carried out extensive model building followed by ab initio quantum chemical calculations. The structures were model built using the software MOLDEN,[13] and ab initio energy minimizations were carried out with 3-21G basis sets[14] using GAMESS-US.[15] The systems characterized were the 2:1 complexes of PY-DMDPM in three possible orientations (Figure 7) along with 1:1 complexes of PY-DMDPM and PY-DMA (not shown in figure). A comparison of the ground-state energies of the three 2:1 complexes shown in Figure 7 indicates that the orientation with PY−PY stacking is extremely unfavorable. The ground-state energy for this complex is ∼ 50 kcal/mol less stable in comparison to the others. This is due to the decrease in stacking interaction during optimization. The ground-state energies of the remaining two favorable complexes differ only by ∼ 2 kcal/mol (Table 3) indicating their similar stability.

We have attempted to understand the excited-state ET mechanism in these complexes using MCSCF[16] wave functions. We used a GUGA option in the MCSCF calculation to probe for single excitation where one of the doubly filled orbitals is converted to two singly occupied active orbitals. The schematic representation of the process (Scheme 3) shows that ET may take place between PY and the donor in several orientations forming the exciplex.

Analyses of the energetics of the complexes and charges on the D and A in ground and excited states of the complexes show that, in all the systems studied, a single ET is possible and the excitations involved are energetically feasible (Table 3). The differences between the ground-state and the excited-state

SCHEME 4



energies for the three different complexes indicate that electron hopping from one DMA unit to the other makes the PY-DMDPM excited states more favorable.

We have also attempted to analyze the two-electron-transfer process in the two favorable PY-DMDPM complexes. As shown in the Scheme 4, the electronic configurations in the various active orbitals are quite different in the two orientations. We however, could not obtain self-consistent wave functions corresponding to any of these situations using normal convergence criteria with our basis sets. We further tried to optimize the wave functions using the ALDET option of MCSCF, where many possible electronic configurations (microstates) are optimized together. Unfortunately, our systems have an extremely large number of such possible configurations and the version of GAMESS does not support it. However, within the software limit we observed several microstates having similar electronic configurations. The schematic description (Scheme 4(b)) clearly indicates that two ET shown in orientation-2 would be energetically more costly as a doubly occupied orbital converts to an unoccupied one. This however, could not be ruled out because of the possibility of electron hopping from the far DMA unit to this unoccupied orbital. Thus we believe that orientation-1 is a more justified situation where both the PYs get excited and two electrons are transferred, one from each $-\mathrm{N(CH_3)_2}$ moiety of DMDPM to PY. Moreover, experimental results predict that the triplex observed was formed by the addition of a second PY to the PY-DMDPM exciplex. As the DMDPM molecule has two donor sites, the most probable representation of the triplex is $\mathrm{PY}^{\delta-}-\mathrm{DMA}^{\delta+}-\mathrm{CH}_2-\mathrm{DMA}^{\delta+}-\mathrm{PY}^{\delta-}$. We could not analyze energies of these, as our optimizations were only for a fraction of all possible microstates.

6. Conclusion

We have tried to characterize the intermediates formed as an outcome of the PET reaction between PY and DMDPM. As DMDPM and DMA molecules are structurally similar, we have always compared our system with the PY-DMA system.

The uniqueness of the PY-DMDPM system lies in the diffusional excursion of the spin-correlated counterparts of RIPs formed on ET. Diffusion dynamics of these RIPs in moderately polar medium (THF-DMF mixture) establishes equilibrium between the contact ion pair, the solvent-separated ion pair, and the free ions in solution. This equilibrium gives rise to all possible structures (I−V) (Scheme 2). However, this does not occur in nonpolar media where contact ion pairs predominate, or in polar media where free ions predominate.

Thus, the dependence of MFE on ϵ proves to be of outstanding importance in our system and helps to identify various structures (I−V) formed in the process of the diffusion of RIPs. Among these, MF resolves the two most favorable complexes, the exciplex and the triplex. This resolution is more pronounced in alcoholic medium where an additional caging effect helps to sort out the desired complexes more effectively.

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References and Notes

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