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Further Studies on Relaxed and Un-Relaxed Exciplexes in Pyrene-N,N-Dimethylaniline System in Benzene-Acetonitrile Binary Solvents

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Abstract

Magnetic field effect (MFE) on pyrene-N,N-dimethylaniline (Py-DMA) exciplex system in benzene-acetonitrile (Bz-ACN) mixtures of varying bulk permittivity (ε) has been studied. The MFE has been wavelength resolved over the emission band of the exciplex along with the measurement of lifetime. The data establishes the concept of formation of two types of exciplexes (Relaxed and Un-relaxed) at higher bulk value of permittivity. At lower value of permittivity when solvent reorganization energy is not so prominent effectively only a single type of exciplex (Relaxed) is formed. The data also indicates that the benzene π cloud favors formation of relaxed exciplex.

Keywords: Relaxed and un-relaxed exciplexes; Wavelength wise resolved magnetic field effect; Life-time signature over the exciplex emission band; Facilitation of electron transfer by benzene

Introduction

Magnetic field effect (MFE) on exciplex luminescence is a well-studied phenomenon [1-4]. In absence of external magnetic field hyperfine interaction mixes the singlet and triplet states of the radical ion pairs (RIP) generated by photo-induced electron transfer (ET) and triplet leakage occurs from the singlet precursor RIP. At saturation value of the external magnetic field $S{\rightarrow}T_{\pm}$ channels are blocked and there is enhancement in singlet state RIP population. As a consequence, population of singlet contact ion pair (CIP) also increases which is responsible for the exciplex luminescence. If ϕ is the luminescence in absence of external magnetic field and the enhancement in saturating field is $\Delta\phi$ then $\Delta\phi/\phi$ is a measure of MFE. Considerable enrichment has been made in literatures in this field recently [5-12]. In a recent paper [13] the MFE ($\Delta\phi/\phi$) have been wavelength wise resolved over the fluorescence band of Py-DMA exciplex system in THF-DMF binary mixtures of varying value of dielectric constant. It has been observed that ($\Delta\phi/\phi$) vs. wavelength (λ) variation changes with change in bulk value of dielectric constant. The lifetime signature (τ) over the emission band of exciplex also is not the same and it depends on the bulk value of dielectric constant. For lower value of dielectric constant ($\varepsilon \leq 9$) the life-time signature is essentially same over the whole exciplex band (homogeneous broadening, single species). This comprises a growth which matches with the pyrene decay at 384 nm and a decay which becomes faster with increase in value of ε. However at higher value of ε at the blue end of the exciplex band (460 nm) the growth is replaced by another short decay. At the middle and the red end of the exciplex band the signature remains the same i.e., we observe a growth and a decay. This observation has been explained on the basis of multiple exciplexes formation at higher dielectric constant (DC, ε). At higher value of ε the solvent reorganization energy is substantial. Under this situation one type of CIP (contact ion pair) is formed which is totally relaxed as far as higher solvation shells are concerned. Due to complete relaxation the exciplex energy is lower and this species emits at the red end of the exciplex band ($\lambda > 500$ nm). It should be noted that electron transfer within the exciplex is likely to be a gradual process as the solvent reorganization follows and induces the overlap of the interacting molecular orbitals and this process can extend to the ns time scale in solvent mixtures [14]. However the lifetime measurements

suggest also formation of a second type of CIP. In this species the charge transfer is instantaneous (not resolved in our TCSPC apparatus) and doesn't wait for complete orbital overlap. Moreover the relaxation of the solvent molecules around this species is also not complete. As a result the exciplex energy is higher and this species emits at the blue end of the exciplex band. This species has been named as 'un-relaxed' exciplex. The MFE ($\Delta\phi/\phi$) signature of these two species are also different. At lower value of dielectric constant where the solvent reorganization energy is low, this differentiation doesn't occur and we have essentially a single type of exciplex, only the relaxed one. It should be noted that this concept has been very successfully used to explain the observed negative MFE [15] in Py-DMA system at very high permittivity (DMSO). However, the establishment of the concept requires further study in other solvent systems. In the present work we have extended this study in case of another aprotic binary solvent mixtures, benzene-acetonitrile, for Py-DMA exciplex system. The data effectively supports the model of formation of relaxed (R) and un-relaxed (U) exciplexes depending on the bulk value of dielectric constant.

Experimental Methods

Pyrene was recrystallized from ethanol-water mixture before use. DMA was received from Sigma-Aldrich and used after vacuum distillation (percent purity>99.5%). All the solvents, benzene and acetonitrile were of HPLC grade (Sigma-Aldrich, percent purity>99.8%). Table 1 depicts the bulk properties of the solvents at standard temperature and pressure. In all the samples pyrene concentration was kept 10^{-4} M and that of DMA was kept at 6×10^{-2} M and these were deoxygenated by slow bubbling of argon over 30

minutes (3.0 ml. of system in cauvette). Each reading was taken from fresh samples and each data point is the average of such 6 readings.

An improved version of phase-locked detection system was employed to monitor the MFE and this is described in detail in our earlier paper [15,16]. The MFE ($\Delta\phi/\phi$) can be detected to a sensitivity of the order of 1 part in 4000 even for a 1 mV value of ϕ (with 1P28 photomultiplier tube biased at -400 V). The spectrophotometer for measurement of lifetime is based on the time correlated single photon counting (TCSPC) technique. The system repetition rate is 1 MHz and the half-width of the instrumental response is of the order of 800 ps. The sample excitation was made at 340 nm and the decay data was convoluted by inbuilt software. The fluorescence of the samples were measured by a Fluoro Max-3 (Jobin Yvon Horiba) spectrophotometer and the excitation wavelength was 345 nm.

Results and Discussion

Figure 1 shows the emission spectra of Py-DMA exciplex {[Py]=10^{-4} M, [DMA]=6 × 10^{-2} M} in benzene-acetonitrile binary mixtures with varying bulk dielectric constant (DC). The average bulk dielectric constant of the mixtures are calculated by the following phenomenological equation:

$$\varepsilon_{m=}\varepsilon_1 x_1 + \varepsilon_2 x_2 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

where ε_i is the dielectric constant of the ith component and x_i is the corresponding volume fraction [17]. Table 1 also depicts the volume compositions of binary solvent for various permittivity values used in the experiment. Viscous drag doesn't follow the equation-1 but under a linear approximation the viscosity of the mixtures will change from 0.57 cP to 0.47 cP and we have neglected the effect of the change in viscosity. Reports show [18] that for Py-DMA system in iso-dielectric (ε=8.4) mixtures this change in viscosity causes an increase in MFE on the order of 0.4% only and therefore the changes observed in our experiment are indeed the outcome of the changes of the bulk permittivity values. The emission gets quenched progressively as dielectric constant is increased along with slight red shift in the peak position. Increase in dielectric constant favors the formation of solvated RIP (radical ion pair) in which non-radiative paths are predominant and CIP luminescence decreases. The peak position of the exciplex luminescence also get red shifted because of the increase of solvent reorganization energy causing a decrease in exciplex energy with increase in bulk permittivity. Figure
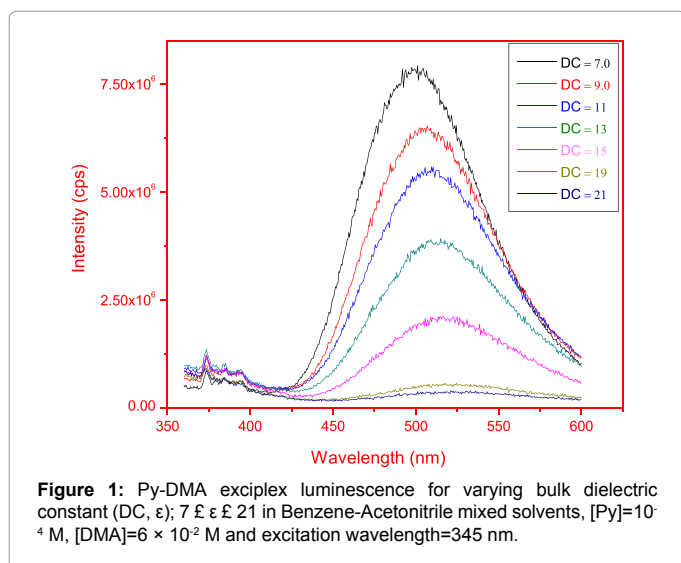
2 depicts the absorption spectra of only pyrene (10^{-4} M) and Py-DMA system ([Py]=10^{-4} M; [DMA]=6 × 10^{-2} M) at bulk permittivity value of 13 of benzene-acetonitrile binary solvent. Absence of any additional structure clearly shows that no ground state complex is forming. We have checked this at other values of permittivity also. Figure 3 depicts the emission spectra of individual pyrene ([Py]=10^{-4} M) and DMA ([DMA]=6 × 10^{-2} M) in benzene and acetonitrile. Table 2 shows the lifetime at pyrene peak (384 nm) and consecutively at blue end (460 nm), peak position (520 nm) and red end (600 nm) of the exciplex band in benzene-acetonitrile binary solvents of varying value of dielectric constant. From Table 2 we observe that lifetime signature is identical over the full exciplex band upto a value of ε=11. This comprises of a growth followed by a decay. This growth (T_1 value at 460 nm, 520 nm and 600 nm) is of the same order of magnitude of the decay at pyrene peak (T_1 value at 384 nm). This effectively indicates formation of relaxed exciplex (R) via quenching of pyrene luminescence by charge transfer process which is a gradual process as the solvent reorganization follows and induces the overlap of the interacting molecular orbitals. The exciplex decay (T_2 at 460 nm, 520 nm and 600 nm) is decreasing with increase in dielectric constant as excepted due to enhanced solvation.

However at higher value of dielectric constant (ε>11) the life-time signature changes substantially. At the red end and the centre of the
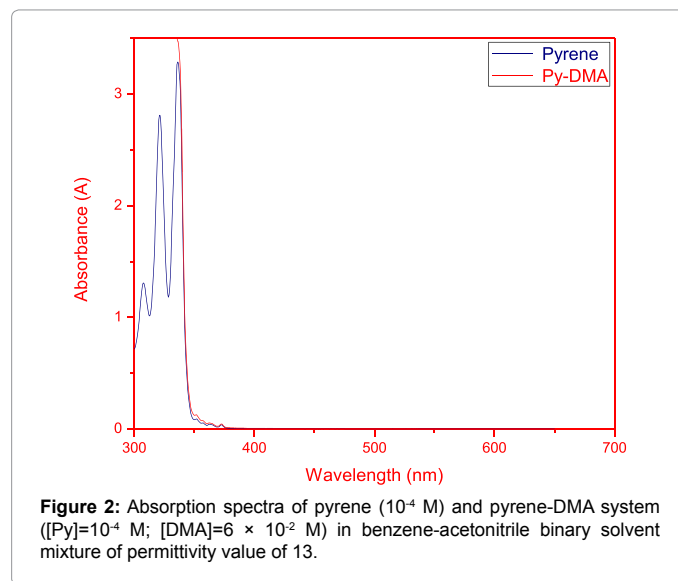
Figure 2: Absorption spectra of pyrene (10^{-4} M) and pyrene-DMA system ([Py]=10^{-4} M; [DMA]=6 × 10^{-2} M) in benzene-acetonitrile binary solvent mixture of permittivity value of 13.

(a)

Solvents	Viscosity (cP)	Dielectric constant	Refractive index
Benzene	0.61	2.27	1.50
Acetonitrile	0.34	37.5	1.34

(b)

ε	Acetonitrile (vol %)	Benzene (vol %)
7	13.43	86.57
9	19.11	80.89
11	24.79	75.21
13	30.46	69.54
15	36.14	63.86
19	47.49	52.51
21	53.17	46.83

Table 1: **(a)** Bulk properties of the solvents used in the experiment **(b)** Volume compositions of binary solvents for the various permittivity (ε) values used in the experiment.

Figure 1: Py-DMA exciplex luminescence for varying bulk dielectric constant (DC, ε); 7 £ ε £ 21 in Benzene-Acetonitrile mixed solvents, [Py]=10^{-4} M, [DMA]=6 × 10^{-2} M and excitation wavelength=345 nm.
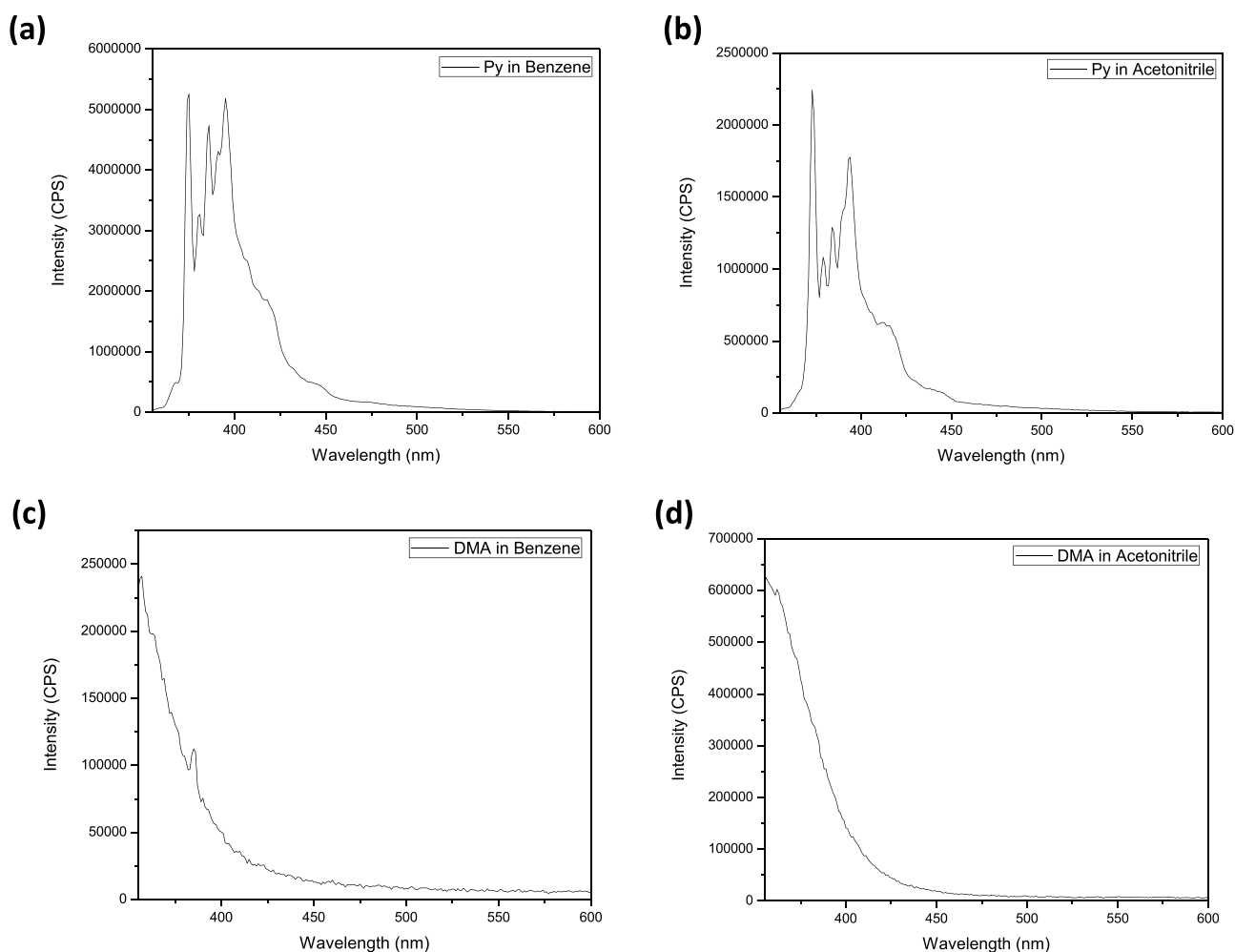
Figure 3: Emission spectra of pyrene ([Py]=10^{-4} M) in benzene (a) and ACN (b) and that of DMA ([DMA]=6 × 10^{-2} M) in benzene (c) and ACN (d). Intensities of the vibration peaks of pyrene show the well known dependence on the local permittivity. DMA emission is far weak than that of pyrene and it is structureless. The spike in (c) is due to the room temperature phosphoresence from solvent benzene itself.

Dielectric Constant	Emission Wavelength			
	384 nm	460 nm	520 nm	600 nm
ε=7.0	T_1=0.84 ns (0.0265) T_2=1.89 ns (0.0234) {1.0141}	T_1=1.17 ns (-0.1625) T_2=84.48 ns (0.2190) {1.0380}	T_1=1.31 ns (-0.1884) T_2=84.81 ns (0.2165) {1.1437}	T_1=1.25 ns (-0.1987) T_2=83.78 ns (0.2149) {1.1050}
ε=9.0	T_1=1.31 ns (0.0359) T_2=2.27 ns (0.0118) {1.0013}	T_1=1.27 ns (-0.1811) T_2=73.43 ns (0.2046) {1.0960}	T_1=1.37 ns (-0.1811) T_2=70.43 ns (0.2094) {1.0868}	T_1=1.48 ns (-0.1678) T_2=70.70 ns (0.2115) {1.0620}
ε=11	T_1=1.09 ns (0.0152) T_2=2.41 ns (0.0080) {0.9216}	T_1=0.77 ns (-0.1723) T_2=73.19 ns (0.2130) {1.0755}	T_1=1.18 ns (-0.1780) T_2=69.83 ns (0.2214) {1.1063}	T_1=1.25 ns (-0.2169) T_2=71.79 ns (0.2301) {1.1415}
ε=13	T_1=0.8 ns (0.0120) T_2=2.11 ns (0.0121) {1.0501}	T_1=28.2 ns (0.1540) T_2=47.14 ns (0.0365) {1.0610}	T_1=1.09 ns (-0.1809) T_2=47.92 ns (0.2127) {1.0374}	T_1=1.01 ns (-0.1728) T_2=47.59 ns (0.2035) {1.0714}
ε=15	T_1=1 ns (0.0165) T_2=2.61 ns (0.0072) {0.9989}	T_1=13.08 ns (0.0382) T_2=27.86 ns (0.1719) {1.0915}	T_1=1.02 ns (-0.1933) T_2=26.59 ns (0.2341) {1.0397}	T_1=0.89 ns (-0.1968) T_2=26.76 ns (0.2353) {1.0557}
ε=19	T_1=1 ns (0.0152) T_2=2.63 ns (0.0085) {1.0324}	T_1=2.66 ns (0.0186) T_2=13.68 ns (0.0444) {0.9930}	T_1=0.99 ns (-0.0522) T_2=13.45 ns (0.0657) {0.9909}	T_1=0.97 ns (-0.0539) T_2=13.53 ns (0.0623) {0.9887}
ε=21	T_1=0.69 ns (0.0116) T_2=1.89 ns (0.0141) {1.0576}	T_1=1.4 ns (0.0331) T_2=6.16 ns (0.0449) {0.9846}	T_1=0.84 ns (-0.0670) T_2=5.96 ns (0.0831) {1.0227}	T_1=0.85 ns (-0.0680) T_2=5.91 ns (0.0811) {0.9929}

Table 2: Life time values over the Py-DMA exciplex band and pyrene monomer emission at 384 nm for varying bulk dielectric constant (ε) of Benzene-Acetonitrile binary mixtures, values inside ( ) and { } represent pre-exponential factor and χ^2 values respectively. (-) pre-exponential factor indicates growth. [Py]:[DMA]=10^{-4} M:6 × 10^{-2} M.

exciplex band the characteristic remains the same. But at the blue end of the band (λ=460 nm) the growth is replaced by another decay (T_1=28 ns at ε=13) which is different from the decay of R (T_2=47 ns at 600 nm, 520 nm and 460 nm). We assign this to the formation of un-relaxed exciplex (U). At higher value of dielectric constant the solvent reorganization energy becomes prominent and the charge transfer distance also increases. We presume that at this condition a new ensemble of exciplex is formed where the charge transfer process is not gradual but instantaneous and these are not relaxed as far as higher solvation shells are concerned. In a sense in this case the charge transfer process doesn't wait for complete orbital overlap. As the solvent relaxation is incomplete the exciplex energy is higher and this species emits at the blue end of the exciplex band. Further increase in the value of ε causes decrease of both the decay rates of U and R. This is because of increase in solvation, as RIP diffuses to the bulk and non-radiative paths are more active.

Figure 4 depicts the MFE ($\Delta\phi/\phi$) on Py-DMA exciplex vs. wavelength (λ) data at varying bulk dielectric constant of benzene-acetonitrile mixtures. It is seen that in case of benzene-acetonitrile mixtures ($\Delta\phi/\phi$) vs λ curves are more or less parallel to X-axis. No appreciable deviation is observed in the range 460 nm to 520 nm at higher value of dielectric constant as seen in case of THF-DMF mixtures [13]. The extent of MFE is similar for relaxed and un-relaxed exciplexes in benzene-acetonitrile mixtures. An interesting information can be gained by plotting ($\Delta\phi/\phi$) vs dielectric constant graphs at a value of λ=460 nm and λ=580 nm. For benzene-acetonitrile mixtures (Figure 5) these two curves are almost identical in contrast to that in THF-DMF mixtures where the peak for λ=460 nm graph occurs at lower value of dielectric constant [13]. In benzene-acetonitrile mixtures, ($\Delta\phi/\phi$) value at ε=21 is the same at λ=460 nm and λ=580 nm and both the curves attain maxima at approximately same value of dielectric constant. ($\Delta\phi/\phi$) vs dielectric constant curves are normally bell shaped and go through a maxima [19]. It is because at low value of dielectric constant the RIPs cannot diffuse to the distance of S-T degeneracy and HFI induced ISC is less, thus ($\Delta\phi/\phi$) value is low. Whereas at high value of dielectric constant, RIPs get more solvated leading to reduced recombination and ($\Delta\phi/\phi$) value is again less. The fact that both the curves pass through the same maxima indirectly indicates that extent of charge transfer is the same for both un-relaxed (λ=460 nm) and relaxed (λ=580 nm) exciplexes in bezene-acetonitrile binary solvents. The similar extent of charge transfer for un-relaxed and relaxed exciplexes in case of benzene-acetonitrile mixtures is surely an anomaly. We think that the planar benzene molecule may get sandwiched between excited pyrene and DMA molecules and its π electron cloud can facilitate electron transfer (ET) [20]. It should be noted that benzene has zero dipole moment and in true sense solvent mediated ET (super-exchange) should not be very effective in benzene. We feel that ET between excited pyrene and DMA is still contact transfer but some way the orientation constraint for ET between them is much reduced in presence of benzene. As a result both the relaxed and un-relaxed exciplexes have similar extent of charge transfer in benzene-acetonitrile binary solvents. Table 3 summarizes the characteristics of MFE in THF-DMF and Bz-ACN binary solvents for Py-DMA exciplex system.

In our previous work [13] to explain the lifetime and MFE data of Py-DMA exciplex system in varying bulk dielectric constant of THF-DMF mixtures we have proposed the model of formation of multiple exciplexes depending on the value of dielectric constant. According to Mataga et al. [21,22] the photo-induced electron transfer in the exciplex system results in a non-relaxed state, a transient ionic complex, followed by orientation relaxation of solvent molecules around it. We presume
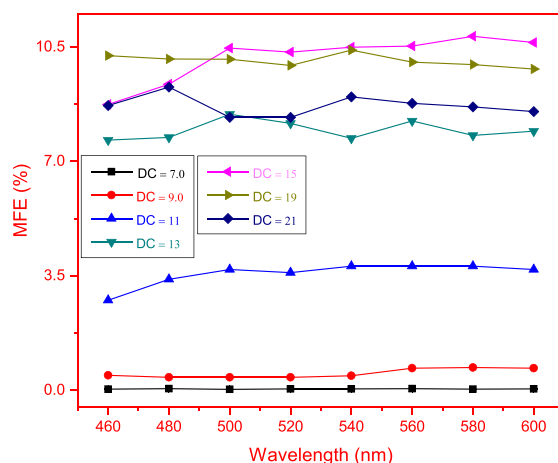

Figure 4: Spectrally resolved MFE on Py-DMA exciplex luminescence for varying bulk dielectric constant (DC, ε); $7 \leq \varepsilon \leq 21$ in benzene-acetonitrile mixture. [Py]=10^{-4} M, [DMA]=6×10^{-2} M. Standard deviation of the data is 7%.
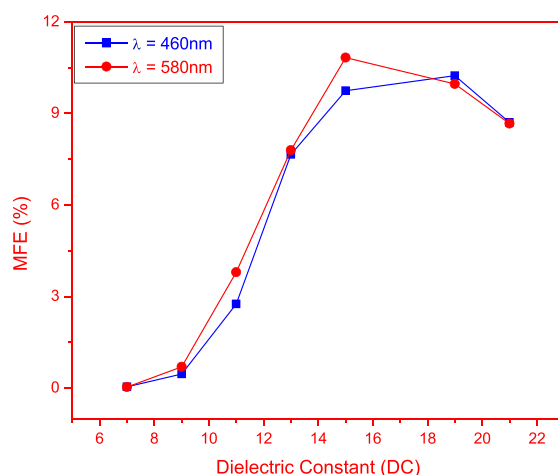

Figure 5: Variation of MFE on Py-DMA exciplex luminescence with bulk dielectric constant (DC) observed at 460 nm and 580 nm in benzene-acetonitrile mixture. Standard deviation of the data is 7%.

Characteristics of MFE of Py-DMA system in THF-DMF binary solvents	Characteristics of MFE of Py-DMA system in Bz-ACN binary solvents
1. Maximum MFE is on the order of 11%.	1. Maximum MFE is slightly less, on the order of 10.5%.
2. MFE vs bulk permittivity signature is distinctly different for Relaxed and Un-relaxed species of exciplexes.	2. MFE vs bulk permittivity signature is almost identical for Relaxed and Un-relaxed species of exciplexes.
3. Peak value of MFE for Relaxed species occurs at ε~15.5 and that for Un-relaxed species occurs at slightly lower value of ε~14.5	3. Peak value of MFE for both type of species occur around the same permittivity on the order of 16.7.
4. MFE of Un-relaxed species falls sharply at higher permittivity than MFE in Relaxed species.	4. MFE of both the species follows the same graph.
5. ET in Relaxed species is greater than that in Un-relaxed species.	5. Extent of ET is identical in both species and it is larger than that in THF-DMF mixtures.

Table 3: Comparison of MFE characteristics of Py-DMA system in THF-DMF and Bz-ACN binary solvents. The difference is mainly caused by the facilitating effect of π cloud of benzene molecule in ET process.

that when this solvent reorganization energy is substantial two types of contact ion pairs (CIP) are formed. In one type the system is totally relaxed as far as formation of higher solvation shells are concerned and we call it 'relaxed exciplex' (R). The exciplex energy is lower because of complete relaxation and this species emits at longer wavelengths ($\lambda > 500$ nm). Electron transfer in case of R is likely to be a gradual process as the solvent reorganization follows and induces the overlap of the interacting molecular orbitals and this process can extend to the ns time scale in solvent mixture [14]. R is thus always associated with a growth. The second type of CIP is not relaxed as far as higher solvation shells are concerned and as the exciplex energy is higher it emits at the blue end of the exciplex band. We call this species 'un-relaxed' exciplex (U). Unlike R the charge transfer process in U is instantaneous (not resolved in our TCSPC apparatus). It should be noted also that in THF/DMF binary mixtures the charge transfer extent in U is lower in comparison to that in R [13]. This is because the Frank-Condon state of the species U is characterized by partial orbital overlap. Thus at higher bulk dielectric constant we have two distinct luminescent exciplexes U and R, each having individual singlet and triplet SSRIP (solvent separated radical ion pair) states and both the species are magnetic field sensitive. The lifetime and MFE data of Py-DMA exciplex system in case of benzene-acetonirile binary solvents also clearly shows the generality of our model.

We now address the very interesting and well established phenomenon of preferential solvation leading to dielectric enrichment around RIP in binary solvent having large difference of permittivity of the constituent solvents [17]. In Figure 1 the peak positions of exciplex emissions (λ_{peak}) at permittivity values 7, 11 and 15 are 496.9 nm, 509.4 nm and 512.3 nm respectively. The potential energy (PE) of the RIP system at a first approximation can be considered to be varying with $1/\varepsilon$ and the exciplex energy is proportional to $1/\lambda_{peak}$. The changes of PE for changes in bulk permittivity from 7→11 and 11→15 are thus 519 au1 (arbitrary unit) and 242 au1 respectively. The corresponding changes in exciplex energies are 49 au2 (arbitrary unit) to 11 au2. This simple empirical analysis indicates that decrease in exciplex energy cannot be accounted by the change in bulk permittivity. In another way, change in local permittivity around the RIP occurs at a faster rate initially and this is exactly the case of dielectric enrichment around the RIP.

Before we close the discussion we would like to point to an observation in Table 3. At 384 nm the pyrene decay is double-exponential. In Table 3 T_1 value at 384 nm matches well with the growth (T_1) of exciplex at $\lambda = 520$ nm, 600 nm. However, we observe a second decay (T_2) at 384 nm which remains around 2 ns over the permittivity range studied. The data do support the model of partial non-specific binding (complex formation) of excited pyrene molecule with solvent molecule ($S-^1Py^*$) in the condensed phase reported earlier [23,24]. We see that in complex excited pyrene, electron transfer process is more facilitated (T_1 at 384 nm) and it is the major channel of exciplex formation.

Conclusion

The work thus clearly shows the formation of multiple types of exciplex (relaxed and un-relaxed) in binary solvents at higher dielectric constant. The first type emits at longer wavelength ($\lambda > 500$ nm) and it is totally relaxed as far as higher solvation shells are concerned. The second type emits at the blue end of the exciplex band (460 nm to 500 nm) and does not undergo solvent relaxation. Further works on different RIP system in different binary and neat solvents (protic and aprotic) have to be carried out for establishing the model.

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