Time-Resolved Emission Studies of Intermolecular Triplet Excimers in Fluid Solutions: Dibenzofuran and Dibenzothiophene Revisited

Xiaohong Wang, Jinquian Tian, William G. Kofron, and Edward C. Lim*,†

Department of Chemistry, The University of Akron, Akron, Ohio 44325-3601

Received: July 13, 1998; In Final Form: October 5, 1998

In fluid solutions at room temperature, the high-purity dibenzofuran (DBF) and dibenzothiophene (DBT) exhibit phosphorescence and delayed fluorescence from monomers as well as intermolecular triplet excimers. The delayed emissions assigned to the excimer are red shifted with respect to the corresponding emissions from the monomers. All four delayed emissions exhibit excitation spectra that are identical with the excitation spectrum of the prompt fluorescence of the corresponding monomer. Consistent with an emission originating from the bimolecular annihilation of the triplet excimers, the delayed excimer fluorescence is spectrally very similar to the normal excimer fluorescence of the compounds, and it decays with a lifetime which is one-half the decay time of the excimer phosphorescence. At longer delay times, where the triplet excimer−monomer equilibration is expected to occur, the ratio of the intensity of the excimer phosphorescence to that of the monomer phosphorescence becomes independent of time. Concomitantly, the lifetimes of the two emissions become identical to each other, as indicated by the very similar lifetimes of the delayed excimer fluorescence and the delayed monomer fluorescence. These results confirm the formation of intermolecular triplet excimers in fluid solutions of these compounds.

Introduction

The triplet excimers of aromatic molecules continue to be a subject of considerable interest as well as challenge. The interest stems from the fact that these species are thought to be stabilized by van der Waals forces,[1,2] rather than by exciton resonance (which stabilizes singlet excimer),[3] and hence are expected to have structures and properties that are substantially different from those of the corresponding singlet excimers.[4,5] However, because of the difficulty of distinguishing excimer phosphorescence from the impurity emission (sensitized by energy transfer from the triplet state of the compound), it has proven to be problematic to identify and characterize aromatic triplet excimers in fluid solutions.[6,7] Nonetheless, time-resolved absorption and emission studies on a number of systems provide strong evidence for the formation of triplet excimers with spectra that are distinctly different from those of the corresponding triplet monomers. The molecular systems reported to exhibit intramolecular triplet excimer formation in fluid solutions are dinaphthylalkanes,[4,8] dicarbazolylakanes,[9] dinaphthyl ether,[10] dinaphthylamine,[11] naphthalene end-labeled poly(ethylene)-glycol,[12] phosphazine polymers with pendant naphthalenes,[13] quinoxaline-annelated dimer,[14] diphenanthrylpropane,[15] and bis-[1-(1-pyrenyl)ethyl]ether.[16] Intermolecular triplet excimer formation in fluid solutions has been reported for carbazole,[17] *N*-ethylcarbazole,[18] dibenzofuran,[17] dibenzothiophene,[17,19] naphthalene (for which there have been disputes[6,7,20]), and for the neat liquid of 1-methylnaphthalene[21] and 1-chloronaphthalene.[21] In addition, there is kinetic evidence for the presence of intermolecular triplet excimers in fluid solutions of aromatic thione[22] and C_{70}.[23] For solid films of polyvinylnaphthalenes,[24,25] poly(vinylcarbazole),[26] and related polymers,[27,28] as well as molecularly doped polymers,[29−31] there have been a number of rather convincing reports of triplet excimer formation. A comprehensive listing of the polymeric systems is given in ref 18.

In previous publications of this series,[17,19] we have described the formation of intermolecular triplet excimers in fluid solutions of dibenzofuran and dibenzothiophene, as evidenced by the appearance of the delayed emissions (delayed fluorescence and phosphorescence) that are distinctly different from those of the corresponding monomer. For dibenzothiophene (DBT), no impurity of any kind was detected and the comparison of the early-time temporal characteristics of the delayed emissions (delayed fluorescence and phosphorescence), with each other and with those of the corresponding monomer emissions, provided compelling evidence for the formation of intermolecular triplet excimers.[19] For dibenzofuran (DBF), however, the sample contained approximately 0.3% anthracene as the major impurity and the structured delayed fluorescence attributed to the intermolecular triplet excimer was observed to be very similar to the prompt fluorescence of anthracene. Thus, although the excitation spectrum of the delayed fluorescence did not reveal features corresponding to the absorption spectrum of anthracene,[17] it is by no means clear that the assignment of the structured delayed fluorescence to the emission arising from the bimolecular annihilation of the triplet excimer is correct. It is therefore essential to reinvestigate the delayed emissions from fluid solutions of DBF using samples that are devoid of the anthracene impurity. Furthermore, for both DBF and DBT, it is very important to establish excimer−monomer equilibration in the triplet manifold by way of delayed emission measurements, to unequivocally distinguish genuine excimer phosphorescence from sensitized phosphorescence of an impurity.

In this paper, we report a time-resolved emission study of DBF samples from which the anthracene impurity has been removed effectively by chemical methods. It is shown that while the longer wavelength (ca. 530 nm) emission assigned to the

---

[†] Holder of the Goodyear Chair in Chemistry at The University of Akron. E-mail: elim@uakron.edu.

10.1021/jp983001a CCC: $18.00

excimer phosphorescence of DBF persists, the structured delayed fluorescence at about 400 nm is absent in the anthracene-free samples. Instead, the delayed fluorescence of DBF, as well as that of DBT, display a structureless feature at about 360 nm which is spectrally very similar to the normal excimer fluorescence of the compounds. Comparison of the temporal characteristics of the delayed excimer fluorescence with those of the excimer phosphorescence demonstrates that the delayed fluorescence arises from the bimolecular annihilation of the triplet excimers. Finally, we demonstrate the occurrence of the excimer−monomer equilibration in the triplet manifold, which is expected to occur in systems forming intermolecular triplet excimers.

Experimental Section

Purity Criterion and Sample Purifications. Although it is not possible to have samples that are completely free of impurity, the acceptable level of solute impurity can be deduced from the requirement that the triplet−triplet energy transfer to impurities must be much slower than the time scale of the spectral measurements that probe the formation and decay of triplet excimers. For typical concentrations of 10^{-4} M and 100 μs time duration of the measurements, the impurity level needs to be substantially less than 0.1% in order for the diffusion-controlled energy transfer (to the impurity) to be at least an order of magnitude slower than the time evolution of the excimer spectra. If, under these conditions, the time-resolved spectra attributable to the triplet excimer appear independent of the nature of the solvent, we consider the assignment reasonable.

Dibenzofuran from Aldrich was treated with maleic anhydride to remove anthracene. In this procedure, a mixture of 0.5 g of dibenzofuran and 0.1 g of maleic anhydride was heated on a steam bath (mixture melted, became pale yellow) for 10 min. Then, 5 mL of 1 M NaOH was added and heating was continued until the solid again melted. The mixture was cooled and shaken with 20 mL of methylene chloride. The organic layer was separated, dried over Na_2SO_4, and evaporated to give 0.41 g of white solid. The procedure (treatment with maleic anhydride, then base, then extraction) was repeated twice. The mixture was almost colorless the third time. The solid was recrystallized from ethanol/water to give 0.31 g (62%) of white plates, mp 81.2−81.5° (starting material melted at 81−82°). GC/MS analyses of the maleic anhydride-treated dibenzofuran showed no trace of anthracene (detection limit 0.02%). GC/MS comparisons also indicate that the only remaining major impurities were fluorene and phenanthrene, present at concentrations of 0.084% and 0.030%, respectively.

Dibenzothiophene, also from Aldrich (99+%), was purified by repeated crystallization from methanol. No impurity of any kind was detected by GC/MS, which places the purity of the sample at greater than 99.98%.

Highest purity solvents from commercial sources were used from the freshly opened bottles without further purification. These include Optima grade isooctane and hexane from Fisher, HPLC grade dichloroethane and cyclohexane from Sigma-Aldrich, HPLC grade ethanol and ethyl acetate from Aldrich, and Spectrophotometric grade methylcyclohexane from Aldrich. Structured “excimer phosphorescence” was sometimes observed from isooctane solution of DBF, which was not observed in other solvents. We suspect that the structured emission is due to the superposition of an emission from solvent impurity and the structureless excimer phosphorescence of DBF.

Apparatus and Procedures. The experimental apparatus and method employed for the time- and frequency-resolved spectral studies of the excimer formation have been described elsewhere.[10] To measure the spectral and temporal characteristics of the laser-induced delayed emissions, the deaerated (by bubbling argon gas) fluid solution of the sample was excited by the unfocused 308 nm output (∼10 Hz) of a Lambda-Physik EMG-50 excimer laser (pulse width ∼20 ns). The emission (fluorescence, delayed fluorescence, and phosphorescence) from the sample was detected by a homemade gated diode-array spectrometer,[10] consisting of an ISA HR-320 monochromator and a PI intensified diode-array detector. For specified delay and sampling times, the data were accumulated over 100 laser shots, and five sets of such measurements averaged to generate the time-resolved emission spectra. The temporal characteristics of the emission were determined by measuring the integrated intensity of the time-resolved spectrum as a function of the delay time between excitation and observation. The maximum temporal resolution of the intensified diode-array apparatus is 5 ns. The delayed emission of the flashlamp(xenon)-excited samples and their excitation spectra were measured using a PTI LS-100-02 spectrophosphorimeter on samples degassed by freeze−pump−thaw methods.

Results and Discussion

Figure 1 shows the time-resolved delayed emission spectra of the flashlamp-excited dibenzofuran (DBF) in isooctane at room temperature. The previously reported[17] structured delayed fluorescence at about 400 nm is absent in the spectra. We must therefore conclude that the structured emission is the sensitized delayed fluorescence of the anthracene impurity. In view of this result and the results on *N*-ethylcarbazole,[18] the structured emission in carbazole,[17] attributed to the delayed excimer fluorescence, also requires reexamination.[32]

As is evident from Figure 1, the delayed emission spectra are composed of four components with intensity maxima (or shoulders) at about 320, 360, 430, and 530 nm. The 320 nm emission, which is most prominent at short delay times (see the lower spectrum), is spectrally very similar to the prompt fluorescence of DBF, and its intensity depends on the square of the incident light intensity (not shown). This indicates that the 320 nm emission is the delayed monomer fluorescence of DBF, arising form the triplet−triplet annihilation of monomers in the lowest triplet state (T_1), i.e., $T_1 + T_1 \rightarrow S_1 + S_0$. At longer delay times, the delayed fluorescence with intensity maximum at about 360 nm gains intensity. The spectral position as well as the spectral shape of the 360 nm emission are very similar to the normal excimer fluorescence of DBF in toluene reported by Horrocks and Brown[33] and to the “excimer fluorescence” from concentrated solutions of DBF in methylcyclohexane (Figure 2). Based on this observation, and the fact that the intensity of the 360 nm emission scales with the square of the incident light intensity (Figure 3), we assign the emission to the delayed excimer fluorescence that results from the bimolecular annihilation of the triplet excimers (T_1'). Whereas the bimolecular annihilation of the monomer triplet state is also known to produce singlet excimer (when it is very stable),[34] the excimer/monomer ratio in the delayed fluorescence is expected to be much larger for the annihilation of the triplet excimers than for the annihilations of the triplet monomers. This is because the excimer annihilation produces a dimeric excited singlet state that can readily transform into the face-to-face geometry of a singlet excimer. Thus, the time evolution of the delayed fluorescence from the largely monomer-like feature to the mostly excimer-like feature can be taken as strong evidence for the formation of intermolecular triplet excimers. The room

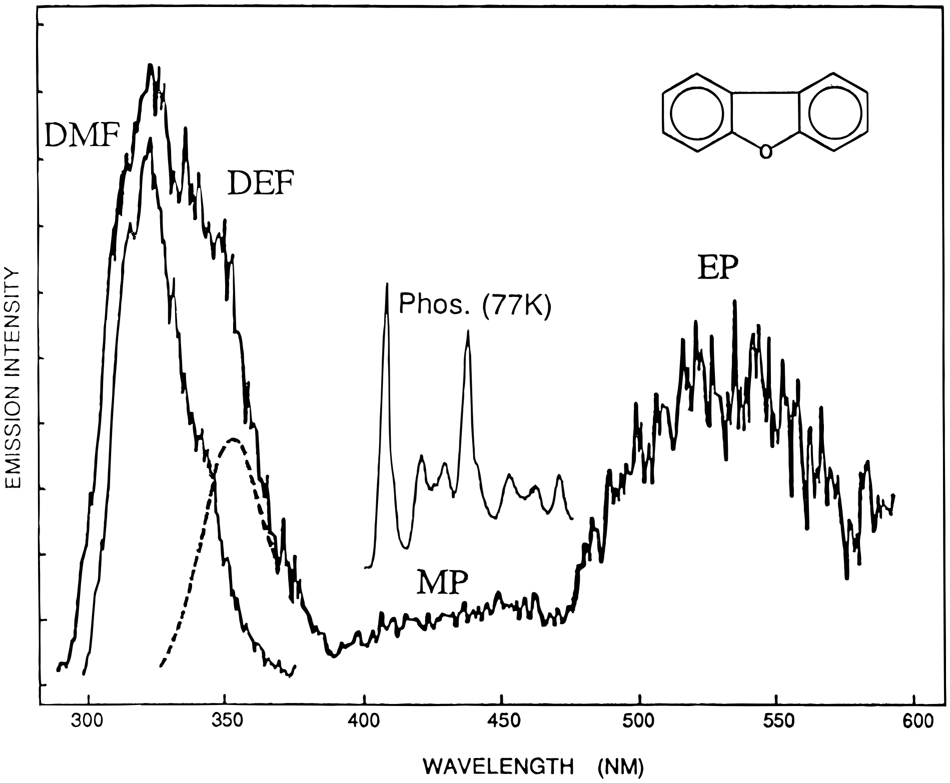


Figure 1. Time-resolved delayed emission spectra of a 1.1 × 10^{-4} M solution of flashlamp-excited dibenzofuran (DBF) in methylcyclohexane at room temperature, measured with a delay time of 100 μs and sampling time of 100 μs. Also shown for comparison is the room-temperature delayed fluorescence spectrum of the same solution recorded at shorter delay (30 μs) and the phosphorescence spectrum of DBF in rigid methylcyclohexane gas at 77 K. MP, EP, DMF, and DEF represent, respectively, monomer phosphorescence, excimer phosphorescence, delayed monomer fluorescence, and delayed excimer fluorescence. The dashed curve represents the spectral shape of the delayed excimer fluorescence, obtained by subtracting the spectrum at shorter delay from that at longer delay. All delayed emission measurements were made using a PTI spectrophosphorimeter (see Experimental Section), whereas the 77 K phosphorescence spectrum was recorded with an Aminco SPF-500 spectrofluorometer.

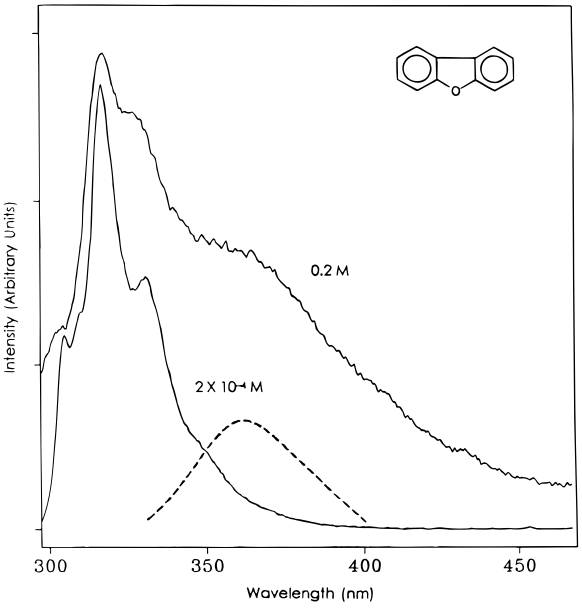


Figure 2. Fluorescence spectra of the concentrated (0.2 M) and dilute (2 × 10^{-4} M) solutions of DBF in methylcyclohexane at room temperature, recorded with an Aminco SPF-500 spectrofluorometer. A structureless excimer fluorescence with intensity maximum at about 360 nm (dashed curve), obtained from the subtraction of the lower concentration spectrum from the higher concentration spectrum, can be identified as the normal excimer fluorescence of DBF (ref 33).

temperature delayed emission at about 430 nm is linearly dependent on the excitation intensity and its spectral position is nearly the same as the low-temperature phosphorescence spectrum of DBF in a rigid glass, also shown in Figure 1. We therefore identify the emission with the phosphorescence of monomeric DBF. The fourth component of the delayed emission at about 530 nm, which is also linear in its dependence on the incident light intensity, can be assigned to the phosphorescence from the intermolecular triplet excimer of DBF, formed by the association of T_1 DBF with a molecule in the ground state (S_0).

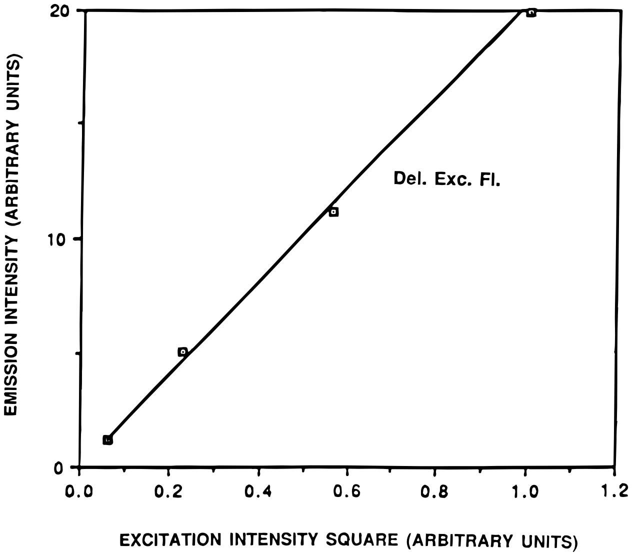


Figure 3. A plot of the intensity of the delayed excimer fluorescence at 360 nm versus the square of the excitation intensity for DBF in methylcyclohexane at room temperature. The experimental conditions were the same as in Figure 1.

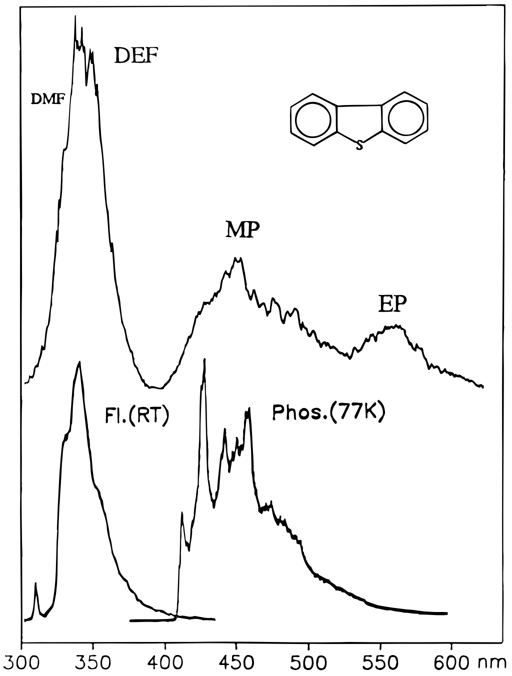


Figure 4. Time-resolved delayed emission spectra (upper trace) of a 9 × 10^{-5} M solution of flashlamp-excited dibenzothiophene (DBT) in isooctane at room temperature, measured with a time delay of 50 μs and a gate width of 10 μs. Also shown for comparison (bottom) are the room-temperature fluorescence spectrum and the 77 K phosphorescence spectrum of the same solution. The notations are the same as in Figure 1.

All four delayed emissions exhibit excitation spectra that correspond to the absorption spectra of the compound.

The time-resolved delayed emission spectra of the flashlamp-excited DBT also exhibit features attributable to the phosphorescence and delayed fluorescence of triplet excimers and triplet monomers, as shown in Figure 4. Consistent with the high quantum yield of phosphorescence in nonpolar glass at 77 K ($\Phi = 0.97$),[35] the monomer phosphorescence of DBT is rather intense even in fluid solution at room temperature. The change of the delayed fluorescence from the monomer-like feature at early times to the excimer-like feature at later times is again evident in time-resolved experiments, as reported in the earlier paper.[19] As in DBF, the spectral position as well as the shape of the delayed excimer fluorescence of DBT is very similar to the normal excimer fluorescence[36] from concentrated solutions of the compound.

In both DBF and DBT, for delay times longer than about 50 μs, the ratio of the intensity of the excimer phosphorescence to that of the monomer phosphorescence remains independent of time, as illustrated for DBT in Figure 5. Since the only species that can be in equilibrium with the triplet monomers are the triplet excimers, these observations rule out the possibility that the emission assigned to the excimer phosphorescence is due to sensitized phosphorescence of an impurity.

As expected, the time-resolved emission spectra of the laser-excited samples of DBF and DBT exhibit strong dependence on laser intensity. Thus, under high-intensity laser excitation, where bimolecular annihilations of the initially formed triplet monomers occur efficiently, the time-resolved emission at short delay time is composed almost exclusively of the delayed monomer fluorescence. The monomer phosphorescence and the excimer phosphorescence are very weak relative to the delayed monomer fluorescence. At longer delay times, or under low-intensity excitation, the emissions attributed to the excimer phosphorescence and delayed excimer fluorescence become clearly discernible, as previously discussed for DBT.[19]

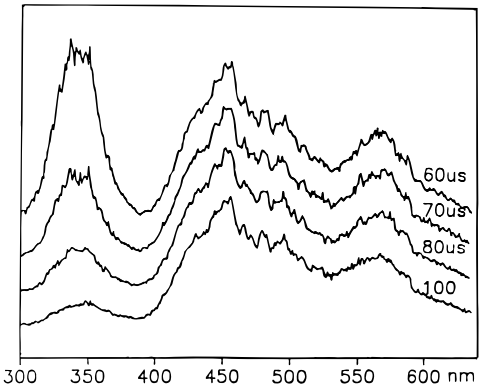


Figure 5. Time-resolved phosphorescence (and delayed fluorescence) of a 9 × 10^{-5} M solution of flashlamp-excited dibenzothiophene in isooctane at room temperature. The spectra for different delay times have been normalized to the same height at the monomer phosphorescence (MP) peak and artificially offset vertically to illustrate that the excimer/monomer ratio in phosphorescence is independent of time for longer delay times. The gate width was 10 μs.

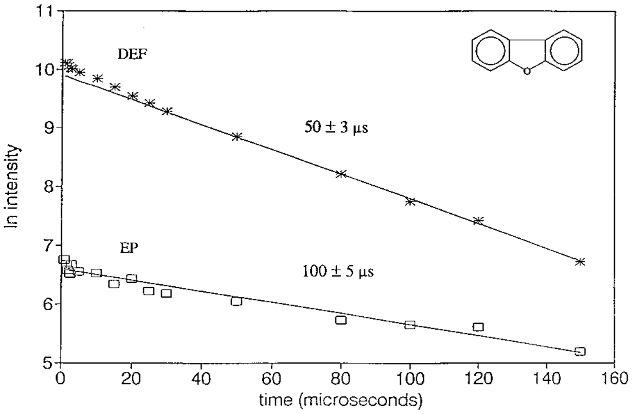


Figure 6. Comparison of the decay time of the delayed excimer fluorescence (DEF) in the region of 347−373 nm (top) with the excimer phosphorescence (EP) in the region of 509−527 nm (bottom) for 8.3 × 10^{-5} M isooctane solution of laser-excited DBF at room temperature. The laser power was 126 μJ, and the gate width was 200 μs. Each data point represents the average of five measurements (see Experimental Section).

The temporal characteristics of the four laser-excited emissions support the spectral assignments. Figure 6 compares the decay characteristics of the excimer phosphorescence of DBF at 530 nm with that of the delayed excimer fluorescence at 360 nm. Consistent with the assignment of the delayed fluorescence to the bimolecular annihilation of the triplet excimers, the delayed excimer fluorescence decays with a lifetime which is one-half of the excimer phosphorescence. Because of the strong spectral overlap between the delayed monomer fluorescence at about 320 nm and the delayed excimer fluorescence at about 360 nm in DBF, the temporal measurement of the excimer emission is difficult at early times (where the emission is very weak compared to the monomer emission). The time dependence of the two delayed fluorescence can however be compared at later times by studying the temporal characteristics of the short and the long wavelength edges of the overlapping emission. The results of such measurements for the 286−301 nm (monomer emission) and 347−373 nm (excimer emission) are shown in Figure 7. It should be noted that whereas the decay of the delayed excimer fluorescence is essentially single exponential, the delayed monomer fluorescence is characterized

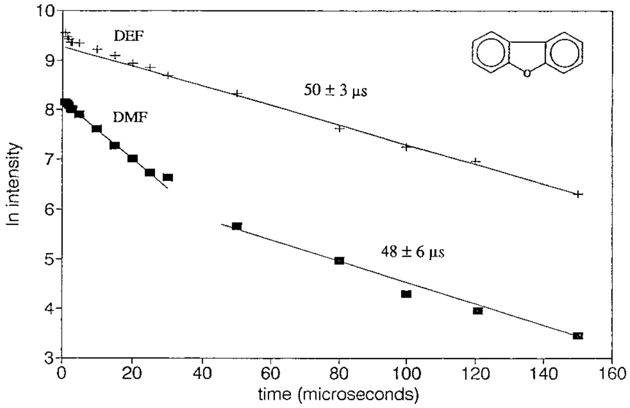
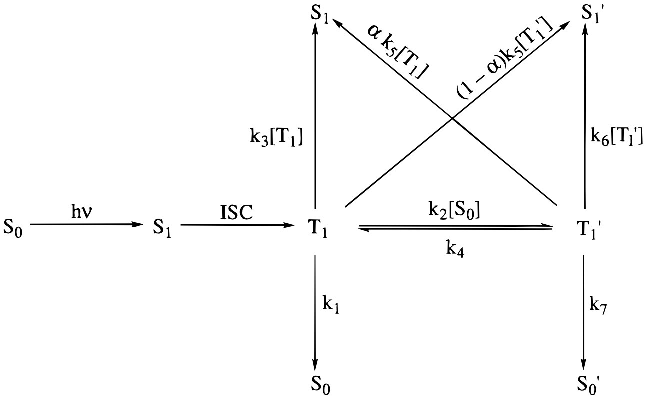


Figure 7. Comparison of the temporal characteristics of the delayed monomer fluorescence (DMF) in the spectral region of 287−301 nm (bottom) with those of the delayed excimer fluorescence (DEF) in the region of 347−373 nm (top) for 8.3 × 10^{-5} M isooctane solution of laser-excited DBF at room temperature. The experimental conditions were the same as in Figure 6.

SCHEME 1



by biexponential decay. For time scales longer than about 50 μs, the two emissions decay with very similar mean lifetimes. The near identity of the decay rates of the two delayed fluorescences is consistent with the monomer−excimer equilibrium in the triplet manifold, which renders the lifetimes of the monomers and excimers identical (vide infra).

The kinetic mechanism presented in Scheme 1 explains the experimental data for DBF and DBT. The triplet monomer (T_1), produced by photoexcitation ($h\nu$) and intersystem crossing (ISC), decays to the ground state by radiative and nonradiative processes, undergoes triplet−triplet annihilation (with rate constant k_3) to form S_1 (lowest excited singlet), and forms triplet excimer T_1' by association with a ground-state (S_0) molecule (with rate constant k_2). The triplet excimer, T_1', in turn decays to the ground state (S_0'), dissociates into T_1 (and S_0), and undergoes bimolecular annihilation (with rate constant k_6) to produce dimeric singlet-state species S_1'. The $T_1 \rightarrow S_0$ and $T_1' \rightarrow S_1'$ radiative transitions correspond to the monomer and excimer phosphorescence, respectively; T_1−T_1 annihilation leads to the delayed monomer fluorescence, and T_1'−T_1' annihilation leads to the delayed excimer fluorescence. Cross annihilation of T_1 and T_1', leading to the formation of S_1 with probability α and S_1' with probability $1 - \alpha$, can also occur.

For times shorter than those required for monomer−excimer equilibration in the triplet manifold, the rate equations for Scheme 1 can be solved under certain conditions. Thus, when the unimolecular decay rates of T_1 and T_1' are much greater than the bimolecular annihilation rates, and when the back dissociation of T_1' is slow as compared to other decay processes for T_1', the solutions of the rate equations lead to[19]

$$[\mathrm{T}_1(t)] = [\mathrm{T}_1]_0\mathrm{e}{-}\lambda_1 t \tag{1}$$

$$[\mathrm{T}_1'(t)] = [\mathrm{T}_1]_0\frac{k_2[\mathrm{S}_0]}{\lambda_1 - k_7}[\mathrm{e}^{-k_7 t} - \mathrm{e}^{-\lambda_1 t}] \tag{2}$$

$$[\mathrm{S}_1(t)] = [\mathrm{T}_1]_0^{\,2}\left[\frac{k_3(\lambda_1 - \lambda_7) - \alpha k_2 k_5[\mathrm{S}_0]}{(\lambda_1 - k_7)(k_0 - 2\lambda_1)}\mathrm{e}^{-2\lambda_1 t} + \frac{\alpha k_2 k_5[\mathrm{S}_0]}{(\lambda_1 - k_7)(k_0 - \lambda_2)}\mathrm{e}^{-\lambda_2 t}\right] \tag{3}$$

$$[\mathrm{S}_1'(t)] = [\mathrm{T}_1]_0^{\,2}\frac{[\mathrm{S}_0]k_2}{(\lambda_1 - k_7)^2}\left[\frac{k_2 k_6[\mathrm{S}_0]}{k_0' - 2k_7}\mathrm{e}^{-2k_7 t} + \frac{k_2 k_6[\mathrm{S}_0] - (1-\alpha)(\lambda_1 - k_7)k_5}{k_0' - 2\lambda_1}\mathrm{e}^{-2\lambda_1 t}\right] \tag{4}$$

where $\lambda_1 = k_1 + k_2[S_0]$, $\lambda_2 = \lambda_1 + k_7$, and k_0 and k'_0 represent the $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ decay rates, respectively. In eq 3, the decay term[19] containing k_0, occurring on a nanosecond time scale, has been omitted, and in eq 4, a small term with (exp$(-\lambda_2 t)$[19] has been deleted for clarity. For DBT, it has been shown[19] that $\lambda_1 > k_7$, $2\lambda_1 > \lambda_2$, $k_3(\lambda_1 - k_7) > \alpha k_2 k_5$, and $k_2 k_6[S_0] < (1 - \alpha)(\lambda_1 - k_7)k_5$.

For times longer than those required for the T_1−T_1' equilibration, the decay rate of the monomer emission (phosphorescence or delayed fluorescence) would be identical to that of the corresponding excimer emission (with rate constant k_7 or $2k_7$). This follows since the rate constant (k_1) for the T_1 decay is expected to be much smaller than that (k_7) for the T_1' decay for both DBF and DBT.[38] Concomitantly, the excimer to monomer intensity ratio would become independent of time.

These considerations, together with eqs 1−4, lead to the following predictions that can be compared to the experiment.

(1) The monomer phosphorescence decays exponentially with rate constant λ_1, whereas the excimer phosphorescence exhibits a buildup to a maximum intensity followed by decay (with rate constant k_7). The build-up rate of the excimer emission is identical to the decay rate of the monomer emission.

(2) The delayed monomer fluorescence decays as a sum of two exponential terms, whereas the delayed excimer fluorescence decays exponentially with rate constant $2k_7$. The slower decaying component of the delayed monomer fluorescence has a rate constant which is identical to that of the delayed excimer fluorescence.

(3) The decay rate of the delayed excimer fluorescence is 2 times that of the excimer phosphorescence.

While prediction 1 could not be tested accurately for DBF due to the low intensity of the monomer phosphorescence (see Figure 1), it has been confirmed by the previous work on DBT.[19] Consistent with prediction 2, the delayed monomer fluorescence of DBF exhibits biexponential decay, as shown in Figure 7. The slower-decaying component indeed has the lifetime that is essentially identical to that of the delayed excimer fluorescence. This observation, and the time invariance of the excimer/monomer intensity ratio at longer delay times (Figure 5), are therefore strong indications for the triplet excimer−monomer equilibration. Since the only species that can be in equilibrium with the triplet monomers are the triplet excimers, these results also rule out sensitized emissions of an impurity as the source of the delayed emissions attributed to the intermolecular triplet excimer. Finally, prediction 3 is confirmed by the results of Figure 6, which demonstrate that the measured lifetime of the excimer phosphorescence is 2 times that of the delayed excimer fluorescence.

Information concerning some of the rate constants can be obtained from the temporal characteristics of the DBF emissions, given in Figures 6 and 7. Thus, the mean lifetime ($1/k_7$) of the excimer phosphorescence, or that ($1/2k_7$) of the delayed excimer fluorescence, yields $k_7 = 1.0 \times 10^4\ \mathrm{s}^{-1}$. The value of λ_1 ($=k_1 + k_2[\mathrm{S}_0]$) can be deduced from the faster decaying component ($e^{-2\lambda_1 t}$) of the delayed monomer fluorescence; i.e., $\lambda_1 = 2.8 \times 10^4\ \mathrm{s}^{-1}$. Combining λ_1 with k_7, we obtain for λ_2 ($=\lambda_1 + k_7$) a value of $3.8 \times 10^4\ \mathrm{s}^{-1}$. Because of the small value[38] of k_1 (vide supra), the measured λ_1 is expected to represent the value of $k_2[\mathrm{S}_0]$. Taking $[\mathrm{S}_0]$ to be roughly 8×10^{-5} M, we obtain $k_2 \approx 3 \times 10^8\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$. Although very approximate, this suggests that the association of the triplet monomer with the ground-state molecule, leading to the formation of the intermolecular triplet excimer, occurs at a rate substantially smaller than that ($\sim 10^{10}\ \mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$) expected for a diffusion-controlled process.

In summary, the results of this study provide strong evidence for the presence of intermolecular triplet excimers in fluid solutions of dibenzofuran and dibenzothiophene. The most compelling of these is that the ratio of the intensity of the monomer phosphorescence to that of "excimer phosphorescence" becomes independent of time for longer delay times. Concomitantly, the lifetimes of the two emissions become identical, as indicated by the very similar lifetimes of the delayed monomer fluorescence and the delayed excimer fluorescence. These observations can only be rationalized if the species giving rise to the "excimer phosphorescence" is the triplet excimer, which exists in equilibrium with the triplet monomer at longer times. Combined with the relevant kinetic data, the excitation spectra that correspond to the absorption spectra, the spectral correspondence between the prompt and the delayed excimer fluorescence, they provide the clearest evidence for the formation of intermolecular triplet excimers. With the delayed emission spectra of the monomeric and excimeric components identified for these compounds, it is now possible to deduce the binding energy of the triplet excimer (vis-à-vis singlet excimer) from the temperature dependence of the excimer/monomer intensity ratio in the phosphorescence spectra. It is also possible to measure the radiative decay rate of the triplet excimer for comparison with that of the triplet monomer, thus providing a direct test of the prediction[37] that the radiative decay rate is much greater for a triplet excimer than for the corresponding triplet monomer. Work along these lines will be undertaken soon.

Acknowledgment. We gratefully acknowledge the critical comments of Dr. Bernhard Nickel which have been an important impetus for the work described in this paper. We are also grateful to Dr. Jianjian Cai and Mr. Wei Xiao for their experimental contributions in the early stage of this work. The financial support for this study was provided by the Office of Basic Energy Sciences of the U.S. Department of Energy.

References and Notes

(1) Lim, B. T.; Lim, E. C. *J. Chem. Phys.* **1983**, *78*, 5262.

(2) Modiano, S. H.; Dresner, J.; Lim, E. C. *Chem. Phys. Lett.* **1992**, *189*, 144.

(3) For reviews, see: Stevens, B. *Adv. Photochem.* **1971**, *8*, 161. Birks, J. B. *Rep. Prog. Phys.* **1975**, *38*, 303.

(4) Lim, E. C. *Acc. Chem. Res.* **1987**, *20*, 8 and references therein.

(5) Lim, E. C.; Locke, R. J.; Lim, B. T.; Fujioka, T.; Iwamura, H. *J. Phys. Chem.* **1987**, *91*, 1298.

(6) Nickel, B.; Rodriguez-Rieto, M. F. *Z. Phys. Chem. (Munich)* **1985**, *150*, 31. Nickel, B.; Rodriguez-Rieto, M. F. *Z. Phys. Chem. (Munich)* **1988**, *146*, 125.

(7) Locke, R. J.; Lim, E. C. *Chem. Phys. Lett.* **1987**, *138*, 489. Locke, R. J.; Lim, E. C. *Chem. Phys. Lett.* **1989**, *160*, 96.

(8) Okajima, S.; Subudhi, P. C.; Lim, E. C. *J. Chem. Phys.* **1977**, *67*, 4611.

(9) Cai, J.; Lim, E. C. *J. Phys. Chem.* **1994**, *98*, 2515.

(10) Modiano, S. H.; Dresner, J.; Lim, E. C. *J. Phys. Chem.* **1991**, *95*, 9144.

(11) Cai, J.; Lim, E. C. *J. Phys. Chem.* **1993**, *97*, 6203.

(12) Tung, C.-H.; Wang, Y.-M. *J. Chem. Soc., Chem. Commun.* **1989**, 1891.

(13) Flamigni, L.; Camaioni, N.; Bortolus, P.; Minto, F.; Gleria *J. Phys. Chem.* **1991**, *95*, 971.

(14) Tero-Kubota, S.; Miyamoto, T.; Akiyama, K.; Ikegami, Y.; Mataka, S.; Tashiro, M. *Chem. Phys. Lett.* **1996**, *249*, 314.

(15) Zachariasse, K. A.; Busse, R.; Schrader, V.; Kühnle, W. *Chem. Phys. Lett.* **1982**, *89*, 303.

(16) Masuhara, J.; Tanaka, J. A.; Mataga, N.; DeSchryver, F. C.; Collart, P. *Polym. J.* **1983**, *15*, 915.

(17) Cai, J.; Lim, E. C. *J. Phys. Chem.* **1992**, *96*, 2935. Cai, J.; Lim, E. C. *J. Chem. Phys.* **1992**, *97*, 3892.

(18) Haggquist, G. W.; Burkhart, R. D. *J. Phys. Chem.* **1993**, *97*, 2576.

(19) Cai, J.; Lim, E. C. *J. Phys. Chem.* **1993**, *97*, 8128.

(20) Hütman, G.; Staerk, H. *J. Phys. Chem.* **1991**, *95*, 4951.

(21) Ohno, T.; Kato, S. *Chem. Lett.* **1976**, 263.

(22) Kozlowski, J.; Maciejewski, A.; Szymanski, M.; Steer, R. P. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 557.

(23) Etherridge, J. T.; Weisman, R. B. *J. Phys. Chem.* **1995**, *99*, 2782.

(24) Kim, N.; Webber, S. E. *Macromolecules* **1980**, *13*, 1233. Pratte, J. F.; Noyes, W. A., Jr.; Webber, S. E. *Polym. Photochem.* **1981**, *1*, 3.

(25) Burkhart, R. D.; Avilés, R. G.; Magrini, K. *Macromolecules* **1981**, *14*, 91. Chakraborty, D. K.; Burkhart, R. D. *J. Phys. Chem.* **1989**, *93*, 4797.

(26) Klöpffeer, W.; Fischer, D. *J. Polym. Sci., Part C* **1973**, *40*, 43.

(27) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2037.

(28) Yokoyama, M.; Masaki, F.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1974**, 372.

(29) Ito, S.; Yamamoto, M.; Liebe, W. R.; Burkhart, R. D.; Wada, Y. *J. Phys. Chem.* **1994**, *98*, 7608.

(30) Abia, A. A.; Burkhart, R. D. *Macromolecules* **1984**, *17*, 2739.

(31) Burkhart, R. D.; Jhon, N.-I. *J. Phys. Chem.* **1991**, *95*, 7189.

(32) *N*-Ethylcarbazole containing a small amount of benzo derivatives of the compound (which are very difficult to remove) is known to produce structured delayed emission similar to that observed from carbazole (ref 18 and a private communication from Professor Richard Burkhart, 1992).

(33) Horrocks, D. L.; Brown, W. G. *Chem. Phys. Lett.* **1970**, *5*, 117.

(34) Parker, C. A. *Photoluminescence of Solutions*; Elservier: London, 1968 and references therein.

(35) Davydov, S. N.; Rodionov, A. N.; Shigorin, D. N.; Syutkina, O. P.; Krasnova, T. L. *Russ. J. Phys. Chem.* **1981**, *55*, 444.

(36) Although the presence of an excimer component is not very obvious in the fluorescence spectrum of concentrated solutions of DBT, the difference spectrum obtained by subtracting the monomer fluorescence from the fluorescence spectrum of the concentrated solution yields a structureless emission band at about 360 nm (intensity maximum), which can be identified as the excimer fluorescence.

(37) Chandra, A. K.; Lim, E. C. *Chem. Phys. Lett.* **1977**, *45*, 7.

(38) The measured quantum yield of the phosphorescence is very close to that of the $S_1 \rightarrow T_1$ intersystem crossing for both DBT and DBF (see ref 35), indicating that the dominant decay channel of the triplet monomer is the $T_1 \rightarrow S_0$ radiative transition. Since the measured lifetime of the phosphorescence at low temperature is 1.3 s for DBT and 4.1 s for DBF (ref 35), one can safely assume that $k_7 \gg k_1$ for these compounds.