

Photoassociation in the lowest triplet state of aromatic molecules: Triplet excimers and exciplexes

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A brief account is given of our recent studies of intramolecular and intermolecular photoassociations in fluid solutions, leading to the formation of triplet excimers and exciplexes.

INTRODUCTION

The question of whether an aromatic molecule in its lowest triplet state can associate with the corresponding ground-state molecule to form a triplet excimer represents a major interest as well as a challenge in molecular photophysics. The challenge comes from the fact that the identification of triplet excimers, based on the measurements of very weak phosphorescence in fluid solutions, requires the high sensitivity of the spectrophosphorimeter as well as high purity of solvents and solutes. This difficulty can be circumvented by measuring the absorption spectrum of the triplet excimers but, because of the insensitivity of the technique, the transient absorption is not a sensitive probe of triplet excimers except when the transition is very strongly allowed. Our recent studies have shown that the formation of triplet excimers of aromatic molecules can be probed easily through the delayed fluorescence that arises from the bimolecular annihilation of the triplet excimers.¹⁻⁵ Both intramolecular triplet excimers of bridged diaryl compounds^{1,4-6} and intermolecular triplet excimers of various aromatic compounds^{2,3,6} have been successfully detected by this method, using conventional spectrofluorimeters of ordinary sensitivity.

The purpose of this talk is to give a brief account of our recent efforts to identify triplet excimers and exciplexes, through the use of the three time-resolved spectroscopic methods (viz., phosphorescence, triplet-triplet absorption and delayed fluorescence). Three cases of the photoassociation in the triplet manifold will be described: 1) intramolecular triplet excimer formation in bridged diaryl compounds, 2) intramolecular triplet exciplex formation in bridged bichromophoric compounds and 3) intermolecular triplet excimer formation in aromatic molecules with permanent dipole moments. For the purpose of illustration, we choose 2,2'-dinaphthylmethane (DNM) or 2,2'-dinaphthyl ether (DNE) as an example of the first case, N-phenyl-2-naphthylamine (PNA) as an example of the second case, and dibenzofuran as an example of the third case. Although chemically unrelated, these molecular systems all exhibit common spectral and temporal characteristics associated with the excimer (or exciplex) formation.

INTRAMOLECULAR TRIPLET EXCIMERS OF BRIDGED DIARYL COMPOUNDS

Figure 1 presents the time-resolved transient absorption spectra (left) and time-resolved emission spectra (right) of degassed solution of DNM in hexane.¹ The transient absorption spectrum at the earliest time delay (1 μ s) is composed of a feature in the region of 350-450 nm and a feature in the region of 500-700 nm. The absorption in the 350-450 nm region is, in turn, composed of a relatively sharp absorption (with intensity maximum at about 420 nm) and a broad feature at slightly longer wavelengths. The sharp feature is very similar to the triplet-triplet absorption spectrum of 2-methylnaphthalene (see the dashed curve at the top), and we assign it to the triplet-triplet absorption spectrum of the non-interacting conformations of the molecule in the triplet state (hereafter simply referred to as triplet monomer). At longer time delays (>50 μ s), only the broad absorption is apparent in the spectral region of 400-450 nm. Since the ratio of the intensity of the broad 400-450 nm feature to that of the 500-700 nm absorption remains independent of the time in the late gated spectra (with delay longer than about 50 μ s), and since the 500-700 nm feature is absent in the transient absorption spectrum of 2-methylnaphthalene, both of these absorption features have been assigned¹ to the transient absorption of the intramolecular triplet excimer of DNM. There is also a corresponding time evolution of the delayed emission spectra. Thus, at short time delay (~300 ns), the spectrum consists of a single emission, which is spectrally identical to the normal, prompt fluorescence (see top right). The intensity of this delayed emission however depends quadratically upon the laser fluence, indicating that the emission is the delayed fluorescence arising from the triplet-triplet annihilation of the monomeric (i.e., non-interacting) conformation of the molecule in the triplet state.¹ With increasing time delay, a new red-shifted emission appears superimposed on the delayed monomer (normal) fluorescence, and it becomes the dominant delayed emission at long delay times (>100 μ s). Since the intensity of this new emission (with excitation spectrum identical to the absorption spectrum) is also proportional to the square of the laser intensity, we have assigned it to the delayed excimer fluorescence arising from the bimolecular annihilation of intramolecular triplet excimers.¹ Similar results were observed for DNE.

If the red-shifted delayed fluorescence is indeed due to the bimolecular annihilation of the intramolecular triplet excimers as we propose, it should be possible to observe phosphorescence from the triplet excimer (which competes with the

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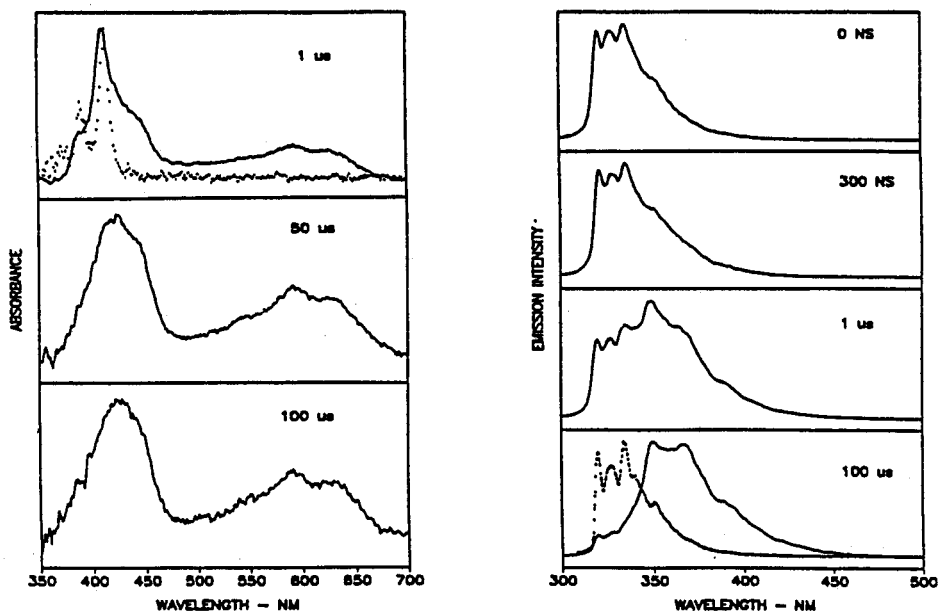


Figure 1. The time-resolved transient absorption spectra, conc. = 5×10^{-4} M (left) and time-resolved delayed fluorescence spectra, conc. = 5×10^{-5} M (right) of degassed solution of 2,2'-DNE in hexane at room temperature.

triplet-triplet annihilation) by making the annihilation process less efficient by reducing the concentration of the triplet-state species. This can be achieved either by reducing the intensity of the excitation source or by decreasing the concentration of the molecules.^{1-4,6,7} Figure 2 shows the effects of excitation intensity (left) and solute concentration (right) on the delayed emission from the degassed solution of DNE in 1,2-dichloroethane. It should be noted that when the intensity of excitation or the concentration of the solute is decreased, a new delayed emission appears at about 520 nm. This new delayed emission is assigned to the excimer phosphorescence.¹ As expected, the excitation spectrum of the excimer phosphorescence is identical with the corresponding absorption spectrum, and its intensity scales linearly with the excitation intensity.

Figure 3 presents the time dependence of the triplet-triplet absorption and that of the delayed fluorescence,⁵ which leads to the following conclusions:

(1) Both the transient absorption and the delayed fluorescence, due to triplet excimers, exhibit a rise time to a maximum intensity followed by a decay, while those due to the triplet monomers (i.e., non-excimeric conformation of the molecule in the triplet state) do not exhibit a rise time,

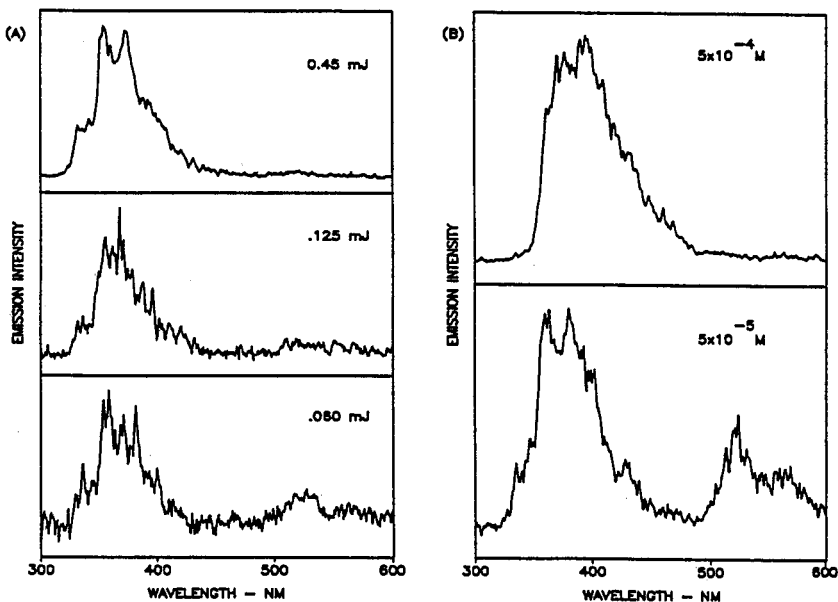


Figure 2. Excitation intensity (left) and concentration (right) dependence of the delayed emission from the degassed solution of DNE in 1,2-dichloroethane at room temperature.

- (2) The rise time of the excimer absorption is equal to the decay time of the monomer absorption, and
 (3) Both the rise and decay times of the delayed excimer fluorescence are approximately half those of the triplet-triplet absorption (or phosphorescence) of the excimer.

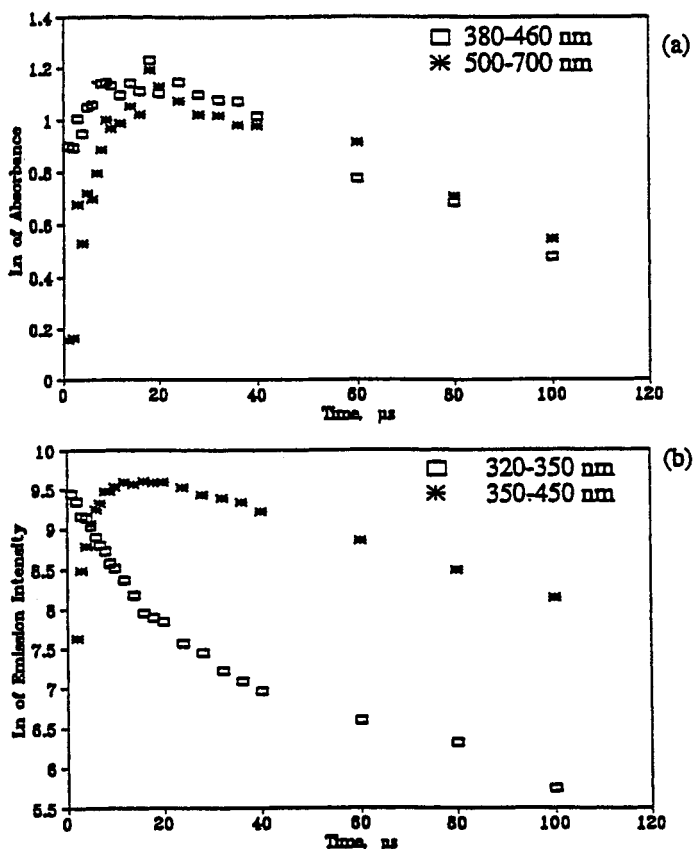


Figure 3. Time dependence of the triplet-triplet absorption (top) and that of the delayed fluorescence (bottom) of degassed solution of DNM in hexane at room temperature. Concentration: 5×10^{-4} M.

As shown elsewhere,^{4,5,7} these results are entirely consistent with the kinetic scheme:



where, 3M represents the non-interacting conformation of the molecule in the triplet state (i.e., triplet monomer), 3M is the intramolecular triplet excimer, and S_1 and S_1' are the excited singlet state of the non-excimeric conformation and that of the excimeric conformation, produced by triplet-triplet annihilation of monomers and excimers, respectively. In the interest of time, we only mention here that, under the experimental conditions employed, reaction schemes (1) - (8) require the rise and decay times of the delayed excimer fluorescence to be one-half of the corresponding quantities in the transient absorption (or phosphorescence) due to the triplet excimers. Furthermore, the rise time of the excimer absorption is expected to be equal to the decay time of the monomer absorption, as observed experimentally.

Observation of very similar results on related molecular systems suggests that the formation of the intramolecular triplet excimer is rather general for bichromophoric systems of the structure, M-X-M, where two identical aromatic moieties are joined to each other by a single bridging group ($X = CH_2, O, NH, \text{etc.}$).⁶

INTRAMOLECULAR TRIPLET EXCIPLEXES IN BRIDGED BICHROMOPHORIC COMPOUNDS

Figure 4 presents the time-resolved delayed fluorescence spectra of degassed solution of N-phenyl-2-naphthylamine (PNA).⁴ As in the case of DNM and DNE, the emission in the short time domain is dominated by the normal delayed fluorescence resulting from the triplet-triplet annihilation of non-excimeric species, while at longer times a red-shifted delayed emission assignable to the delayed exciplex fluorescence becomes prominent. The intensity of the delayed exciplex fluorescence is proportional to the square of the excitation intensity (see Figure 5).⁴ When the excitation intensity is reduced, still another delayed emission appears at about 575 nm, whose intensity scales linearly with the excitation intensity.⁴ We assign this emission to the phosphorescence from the intramolecular triplet exciplex. The excitation spectra of the delayed exciplex fluorescence as well as that of the exciplex phosphorescence are identical to the absorption spectrum of PNA (see Figure 6).⁴ Since the lowest excited states (singlet and triplet) of PNA are locally excited states in which the excitation is largely localized on the naphthalene-NH moiety,⁴ the formation of the intramolecular triplet exciplex is envisioned to involve reorientation of the phenyl group with respect to the "naphthylamine" moiety. Consistent with a large-amplitude motion of the phenyl group with respect to the Np-NH moiety, expected for the intramolecular triplet exciplex formation, the appearance time of the delayed exciplex fluorescence (which is a measure of the formation time of the exciplex) is considerably longer in solvents of high viscosity.⁴

The assignments of the "delayed exciplex fluorescence" and the "exciplex phosphorescence" to the intramolecular triplet exciplexes are supported by the observation that the lifetime of the "exciplex phosphorescence", measured during the time interval in which the normal delayed fluorescence is very weak, is approximately two times that of the "delayed exciplex fluorescence", consistent with the reaction schemes (in the previous section).⁴ As in DNM and DNE, these results provide strong dynamical support for the assignment of both emissions to the intramolecular triplet exciplex of PNA.

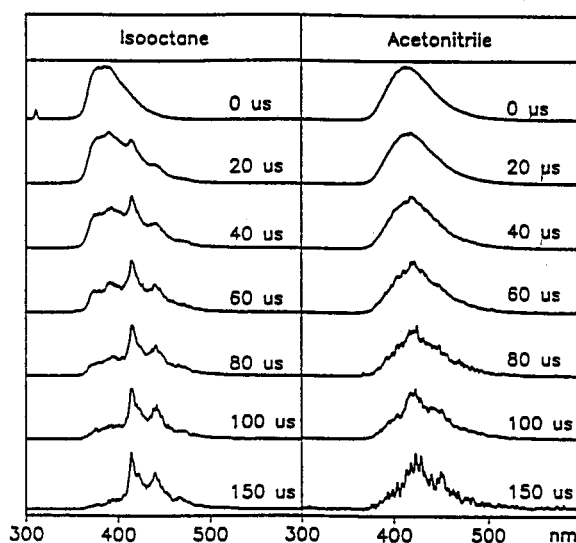


Figure 4. Time-resolved delayed fluorescence spectra of the degassed solution of PNA at room temperature. Concentration: 1.0×10^{-4} M.

INTERMOLECULAR TRIPLET EXCIMERS OF AROMATIC MOLECULES WITH PERMANENT DIPOLE MOMENTS

The triplet excimers of aromatic molecules are expected to be stabilized largely by van der Waals forces (electrostatic, induction and dispersion forces).⁸⁻¹⁰ Since these forces are stronger for molecules with dipole moments than those with only quadrupole moments, the formation of triplet excimers may be expected to be more efficient for aromatic molecules with permanent dipole moments. Consistent with this supposition, we have recently observed efficient formation of intermolecular triplet excimer from fluid solutions of a number of polar aromatic compounds.^{3,7}

Figure 7 presents the time-resolved delayed fluorescence spectra of dibenzofuran, in methylcyclohexane at room temperature, taken under high-intensity (left) and low-intensity (right) excitations.^{2,3} As in the previous examples, the emission appearing in the short time domain is the normal delayed fluorescence resulting from the triplet-triplet annihilation of monomeric species. At longer times the structured delayed fluorescence again appears, superimposed with the delayed monomer emission. The excitation spectrum, dependence of its intensity on the excitation fluence, as well as its temporal characteristics, all indicate that the red-shifted, structured emission is the delayed excimer fluorescence arising from the bimolecular annihilation of two intermolecular triplet excimers (each formed by the association of a molecule in its lowest triplet state with a molecule in its ground electronic state).³ As in the case of DNM, DNE and PNA, excimer phosphorescence can be observed from these compounds when the annihilation process is made less efficient by decreasing the excitation intensity (and hence the concentration of the triplet-state species).^{2,3} These results are remarkably similar to those observed for various bridged bichromophoric compounds exhibiting the formation of intramolecular triplet excimers (or exciplexes). Consistent with the sequence of photoprocesses in steps (1) - (8), the lifetime of the excimer phosphorescence, measured during the time interval in which the delayed normal fluorescence is very weak, is approximately two times that of the delayed excimer fluorescence.³ Finally, the intermolecular character of the triplet excimers is strongly supported by the observation that the intensity of the delayed excimer fluorescence increases relative to that of the delayed monomer

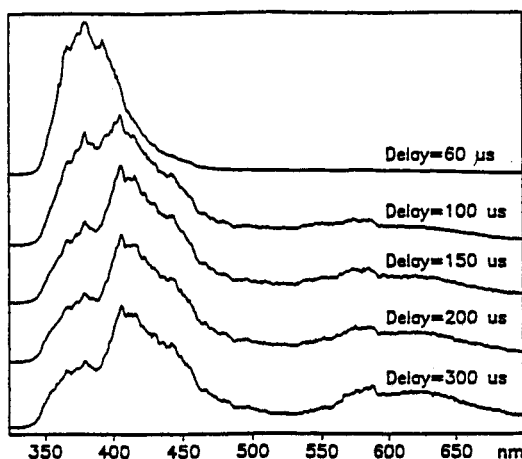


Figure 5. Time-resolved delayed emission spectra of the lamp-excited PNA in isooctane at room temperature. Concentration: 1.0×10^{-4} M.

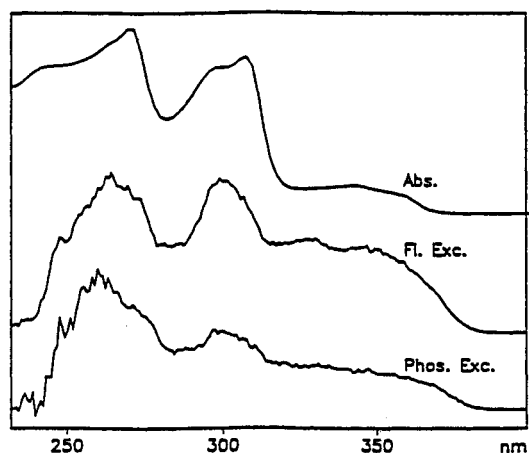


Figure 6. Comparison of the excitation spectrum of the delayed exciplex fluorescence and that of the exciplex phosphorescence with the absorption spectrum of PNA, all in isooctane at room temperature.

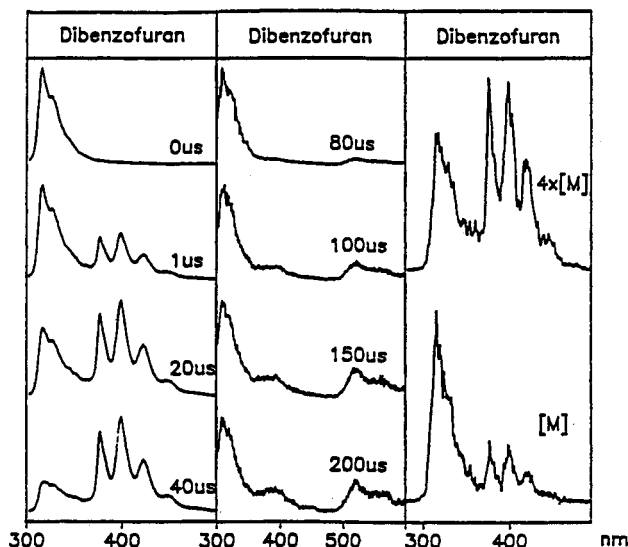


Figure 7. Time-resolved delayed fluorescence spectra of dibenzofuran in methylcyclohexane at room temperature, taken under high-intensity (left) and low-intensity (middle) excitations. The figure on the right presents the dependence of the intensity of the delayed excimer fluorescence and that of the delayed monomer fluorescence on solute concentration.

fluorescence as the ground-state concentration of the solute, $[S_0]$, is increased (Figure 7 right).³ This is to be expected for intermolecular triplet excimers, as the intensity of the delayed excimer fluorescence scales with $[^3E]^2$, or $[^3M]^2[S_0]^2$, while that of the delayed monomer fluorescence scales with $[^3M]^2$. Observation of similar results in other polar aromatic molecules⁷ suggests that the formation of intermolecular triplet excimer may be general for molecules with substantial dipole moments.

CONFORMATIONAL SIMILARITY BETWEEN TRIPLET EXCIMER (OR EXCIPLEX) AND THE CORRESPONDING-GROUND-STATE VAN DER WAALS DIMER (OR COMPLEX)

The striking spectral feature of the delayed excimer fluorescence common to all the molecular systems is the appearance of a clear vibrational structure in the spectrum. In general, excimer fluorescence is broad and structureless owing to the repulsive character of the ground state in which the radiative transition terminates. The fact that the delayed excimer fluorescence of our molecular systems exhibit vibrational structures therefore implies that the annihilation-created excimer (or exciplex) has a local minimum in the ground electronic state, with intermolecular coordinates that are similar in the ground and the lowest excited single states.¹¹ The local minimum could be the ground-state van der Waals dimer (or complex), which like the corresponding triplet excimer, owe its existence in van der Waals forces. If this supposition is correct, the excited singlet state created by the bimolecular annihilation of the triplet excimers (or exciplexes) may be structurally similar to the excited state of the van der Waals molecule, so that the excimer fluorescence may closely mimic the prompt fluorescence of the ground-state-formed van der Waals dimer (or complex). It is therefore significant that the molecular systems exhibiting formation of triplet excimers (or exciplexes) all tend to form ground-state van der Waals dimers or (complexes) when the solution containing them is cooled to lower temperatures.^{1-4,6,7,10} This allows the comparison of the prompt fluorescence of the van der Waals molecules, trapped in glass-forming solvents at low temperature, with the

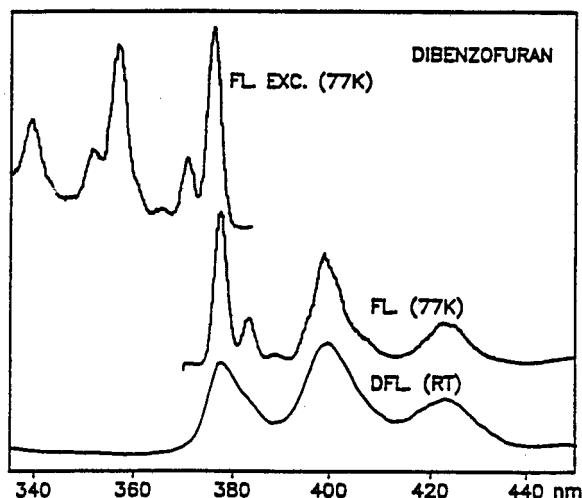


Figure 8. Comparison of the prompt fluorescence of the ground-state-formed van der Waals dimer of dibenzofuran in isopentane glass at 77 K with the delayed fluorescence due to bimolecular annihilation of the triplet excimer in isooctane at room temperature. Also shown in the figure is the fluorescence excitation spectrum of the van der Waals dimer.

corresponding delayed fluorescence produced by bimolecular annihilation of the triplet excimers. This comparison^{3,4,10} which is illustrated for dibenzofuran in Figure 8, demonstrates that the prompt fluorescence of the ground-state-formed van der Waals dimer is essentially identical to the corresponding delayed excimer fluorescence in fluid solution at room temperature. Since the excited singlet state produced by the triplet-triplet annihilation of the excimers is expected to reflect the conformation of the triplet excimer, the close resemblance of the two emission spectra suggests that the conformation of the triplet excimer is similar to that of the ground-state dimer, as predicted some time ago.^{8,9} Very similar results were also obtained for DNM,¹⁰ PNA,⁴ as well as for carbazole⁷ and dibenzothiophene.⁷

Despite the existence at low temperature of the ground-state van der Waals dimer closely related to the corresponding triplet excimer, the term "excimer" is still valid in describing excited-state dimers of these species at room temperature, as there is little spectroscopic evidence for the formation of the stable ground-state van der Waals dimers at ambient temperature. The occurrence of the triplet excimer formation and the near-absence of the ground-state dimer formation at ambient temperature are consistent with the expectation that the binding energy of triplet excimer is greater than that of the corresponding ground-state dimer due to the greater van der Waals forces associated with the excimer formation.

CONCLUSION

Triplet excimers can be identified by their characteristic phosphorescence and triplet-triplet absorption, as well as by the delayed fluorescence arising from the bimolecular annihilation of the species. Although each method has its own inherent shortcoming, collectively they provide strong diagnostic tool for identifying and characterizing triplet excimers. Thus, while the insensitivity of the absorption technique is a disadvantage, it is also an advantage since the method is least influenced by the presence of impurity (only when present in large quantity can impurity be detected by the absorption method). The time-resolved emission and absorption studies presented here provide self-consistent, compelling evidence for the formation of triplet excimers (and exciplexes) in fluids solutions of a variety of aromatic molecules. The results also provide experimental evidence that triplet excimers of aromatic hydrocarbons are stabilized largely by van der Waals forces.

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