Characterization of the Triplet–Triplet Annihilation Process of Pyrene and Several Derivatives under Laser Excitation[1]

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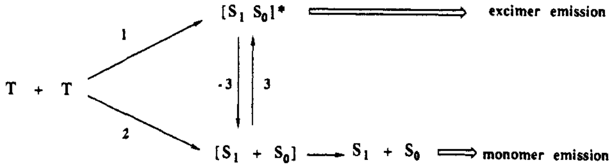
Abstract: Under conditions of pulsed laser excitation, pyrene and several of its substituted derivatives readily show P-type delayed fluorescence originating from triplet–triplet annihilation (TTA); this emission shows high contributions from excimer emission under conditions where only monomer fluorescence is observed from singlet states formed by direct excitation by the laser pulse (prompt emission). The effect observed in the delayed fluorescence results from the formation via TTA of excited singlet states (monomer or excimer) in a solvent cage that *always* contains two pyrene molecules. TTA rate constants approach diffusion control when spin-statistics are taken into account. Substituted pyrenes show wide variations in the excimer-to-monomer ratio for the delayed fluorescence. In particular, the ratio for pyrenedodecanoic acid (PDA) in polar solvents is similar to dodecylpyrene (DPY) in cyclohexane, but the ratio is much higher for PDA in nonpolar solvents. The effect is attributed to carboxylic association during the TTA encounter that assists excimer formation. P-type delayed fluorescence in pyrenes may prove useful as a probe for mobility in organized systems.

P-type delayed fluorescence in solution originates via the interaction of two triplet-state molecules in a process normally described as triplet–triplet annihilation (TTA). With long-lived triplets, such as those derived from aromatic hydrocarbons, and under conditions of pulsed laser excitation, TTA can be an important form of triplet decay. In the case of pyrene and its derivatives, fluorescence arises from two different species: the monomer and the excimer; the latter is an excited dimer normally produced by interaction of the excited monomer with a ground-state molecule. As a result, the excimer-to-monomer (E/M) ratio of emission intensities for the prompt fluorescence is concentration dependent and tends to zero at low concentrations. Typically, no prompt excimer emission can be detected at concentrations $<5 \times 10^{-5}$ M. We use the term prompt emission to refer to fluorescence from singlet states formed by direct excitation by the laser pulse.

It has been known for over 20 years that the delayed emission from pyrene leads to a higher E/M ratio than its prompt luminescence.[4-18] From a purely descriptive point of view, and given the bimolecular nature of the process, in the case of TTA there will always be two pyrene molecules in the solvent cage in which the fluorescent species is formed, and thus, one can anticipate an enhancement of the excimer yield under these conditions. An obvious corollary of the observations mentioned above is that the pyrene monomer and excimer cannot be in equilibrium, since if this was the case it would not matter from which side (i.e. monomer or excimer) the equilibrium was approached and the E/M ratio should be equal for the prompt and delayed emissions.

Scheme I



The different pathways that could lead to excimers in the interaction of two triplets are outlined in Scheme I. There are three distinct possibilities for excimer formation: (i) concomitant formation of excimers and monomers (pathways 1 and 2 are operative); (ii) formation of excimers only, which would subsequently dissociate into monomers (pathways 1 and −3 are operative), and (iii) exclusive formation of monomers that would give excimers by reassociation with the ground-state molecule in the solvent cage (pathways 2 and 3). Several authors addressed these different possibilities.[6-15]

In the earlier studies low-irradiation doses (i.e. lamp) and relatively high ground-state concentrations were employed. For these reasons some excimeric emission was always observed in the prompt fluorescence,while the delayed emission followed a first-order (i.e. monoexponential) decay and did not contain any kinetic information about the annihilation rate. At the low triplet concentrations achieved under lamp irradiation the second-order component is only a minor perturbation relative to the dominant first-order decay. On the other hand, in the laser excitation of dilute pyrene solutions employed in our work, high triplet concentrations are obtained. Thus, no excimeric emission is observed in the prompt fluorescence, as much lower pyrene concentrations were used, and the decay kinetics of the delayed emission incorporates an important second-order component from which the TTA rate constant can be obtained.

The delayed fluorescence from pyrene has been the subject of studies that include its viscosity, temperature,[8,10] and magnetic field dependence.[14-17] Surprisingly, pyrene derivatives do not appear to have been examined. In this paper the TTA of pyrenes was studied under laser excitation, in order to obtain additional information, including the TTA rate constants. For the various pyrene derivatives investigated it was observed that the delayed fluorescence is strongly dependent on the substitution, and for some molecules on the solvent used.

Results

By employing laser excitation and detection by a gated-intensified optical multichannel analyzer (OMA) it is nowadays possible to carry out this type of work under conditions where the prompt emission from pyrene contains no detectable excimer fluorescence.

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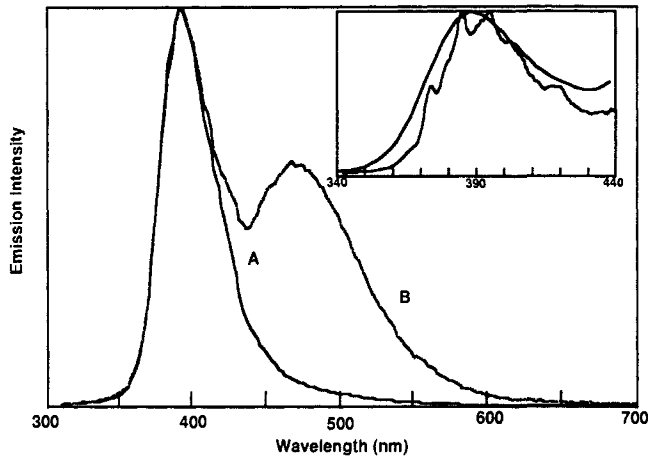

Figure 1. Prompt (A) (150-ns delay, 20-ns gate) and delayed (B) (10-μs delay and 600-ns gate) fluorescence of pyrene (50 μM) in cyclohexane. The spectra were normalized for the monomer emission. The prompt fluorescence spectrum is the same when collected with a 20-ns or a 3.0-μs gate; in the latter the total prompt emission is measured. The insert shows the delayed emission in the spectral region of the monomer with two different gratings on the spectrograph.

In earlier work the "true" TTA excimeric excess was normally determined via an extrapolation to zero pyrene concentration;[8] our experiments are equivalent to working at the intercept conditions of earlier work. Figure 1 compares prompt and delayed emission from pyrene in cyclohexane. The reader familiar with pyrene monomer fluorescence spectra in the 400-nm region will note the absence of vibrational structure in Figure 1. We have chosen to work under conditions of rather poor spectral resolution in order to maximize our ability to detect weak signals, to employ very short (frequently 20 ns) OMA detection gates, and to obtain simultaneous spectra of the monomer and excimer. The inset shows the monomer region of the spectrum obtained under conditions of better spectral resolution (but where the excimer cannot be monitored in the same OMA scan), where the structure is evident.

Figure 1 shows that the pyrene monomer emission is identical regardless of its origin (prompt or delayed). The intensity of the prompt emission is much higher than the one corresponding to the delayed fluorescence, and prompt emission contributes to the measured monomer emission intensity up to ~3.0 μs (~$8\tau_f$, where τ_f is the singlet lifetime) after the laser pulse. For longer delays the excimer-to-monomer (E/M) emission intensity ratio is constant, showing that only delayed fluorescence is being monitored. For detection delays >3 μs the delayed emission E/M intensity ratio does not depend on the magnitude of the gate width for data collection, which was varied between 20 and 1000 ns. As the pyrene monomer and excimer have different emission lifetimes (420 (vide infra) and 65 ns,[19] respectively) their concentration ratio, as monitored by delayed fluorescence, must thus be constant. Therefore, the rate-limiting step in the TTA process is the triplet decay, and processes after the interaction of the two triplet molecules (i.e. excimer formation or dissociation) are much faster.

The E/M ratios were measured by integrating the emission in the 370–410- and 500–600-nm ranges for the monomer and excimer, respectively, wavelength ranges where these emissions do not overlap extensively. No correction for the wavelength dependence of OMA response was normally performed, as the corrections are substantially less than 20%. This E/M ratio is slightly dependent on the precision of the OMA wavelength calibration, as only fractions of the spectra are being integrated. In some instances, the intensity ratio of the excimer-to-monomer maxima ($(E/M)_{max}$) will be reported, as this value is independent on the OMA calibration and can be used for comparisons of values obtained with different experimental setups. The $(E/M)_{max}$ for pyrene in cyclohexane is 0.67 ± 0.09 (average of six experiments).[20]

The delayed emission decay was monitored by recording spectra at different times following laser excitation. This intensity follows a complex dependence with time, having both second- and first-order components. In fact, this dependence only simplifies if the second-order decay via TTA is a minor perturbation on the dominant first-order mode of decay. Under these conditions the decay is monoexponential and the delayed emission lifetime is one-half of the triplet lifetime; all of the work in the late 1960s was carried out under conditions where this criterion was met. Of course, the consequence of this simplification is that the data contain no information on the kinetics of the TTA process. In contrast, pulsed laser excitation leads to relatively high triplet concentration, and the time evolution of the emission intensity contains information on the TTA rate constant. In our case, the triplet states (T) decay by mixed first- and second-order kinetics

$$\mathrm{T} \xrightarrow{k_1} \text{decay} \tag{1}$$

$$\mathrm{T} + \mathrm{T} \xrightarrow{2k_{\mathrm{TTA}}} \text{decay and emission} \tag{2}$$

where k_1 is the first-order rate constant, which incorporates the first-order decay and any impurity quenching process (normally due to the presence of traces of oxygen) which is constant over the experiment, and k_{TTA} is the TTA rate constant. The rate law for the triplet decay is given by

$$\frac{\mathrm{d}[\mathrm{T}]}{\mathrm{d}t} = -k_1[\mathrm{T}] - 2k_{\mathrm{TTA}}[\mathrm{T}]^2 \tag{3}$$

Since delayed emission, which is a probe for the triplet concentration, originates from reaction 2, we expect a quadratic dependence of the emission intensity (I_t) at time t, i.e.

$$I_t = \alpha[\mathrm{T}]_t^2 \tag{4}$$

which, following detailed kinetic analysis, leads to

$$I_t = \alpha\left(\frac{[\mathrm{T}]_0 e^{-k_1 t}}{1 + (1 - e^{-k_1 t})\dfrac{2k_{\mathrm{TTA}}}{k_1}[\mathrm{T}]_0}\right)^2 \tag{5}$$

where $[\mathrm{T}]_0$ is the initial triplet concentration (at the time of laser excitation) and α an experimental parameter that incorporates the monomer and excimer emission quantum yields, the quantum yield of singlet formation in the TTA process, and the OMA actual sensitivity, which is a direct function of its quantum efficiency and alignment.

Accurate values of $2k_{\mathrm{TTA}}$ could not be obtained directly from the triplet pyrene transient absorption data due to poor signal/noise ratio for this absorption in the case of OMA detection and to interference from pyrene prompt fluorescence at the wavelength (415 nm) where the triplet–triplet absorption was monitored with a photomultiplier detection system. Delayed fluorescence intensities are measured with a greater precision.

The experimental data for the delayed fluorescence were fitted to eq 5 (Figure 2) by a computer program in which the values of α, k_1, and $2k_{\mathrm{TTA}}$ were floated. The value of $[\mathrm{T}]_0$ was determined from OMA transient absorption measurements under the same conditions (i.e. alignment and laser power) as emission measurements and is based on ϵ = 30400 M^{-1} cm^{-1} at 413 nm for pyrene in cyclohexane[21] and an optical pathlength of 2.3 mm (see Experimental Section). After an initial range is set for the parameters to be floated, the program carries out a search to locate the minimum in the sum of the square of the residuals (see Experimental Section). In fitting the data to eq 5 it is important to obtain precise values at long delays that define the accuracy

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(20) The dispersion in the $(E/M)_{max}$ values is probably due to different alignments of the OMA optical bench. The focussing of the incoming light on the OMA is critical, and small differences of the response at different wavelength can be observed.

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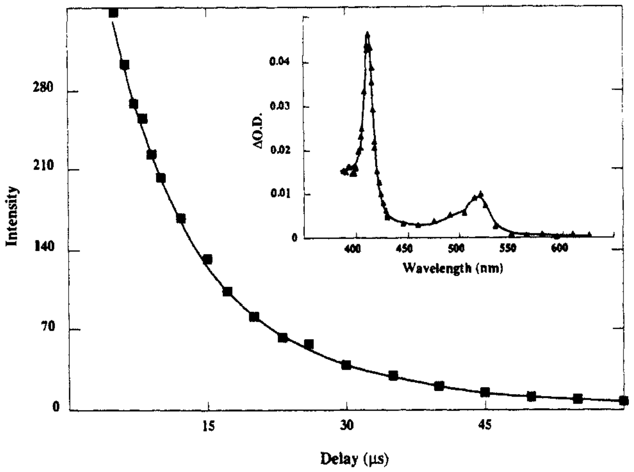


Figure 2. Experimental data (■) and computer-fittted decay (—) for the delayed fluorescence of pyrene (50 µM) in dodecane. The insert shows the transient absorption spectra of pyrene in cyclohexane.

Table I. TTA Rate Constants and $(E/M)_{max}$ Values for Pyrene and Derivatives in Different Solvents

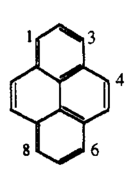
compd	solvent	viscosity, cP	$2k_{TTA} \times 10^{-9}$,[a] $M^{-1}\ s^{-1}$	$(2k_{TTA})_{dif} \times 10^{-9}$,[b] $M^{-1}\ s^{-1}$	$(E/M)_{max}$[c]
pyrene	cyclohexane	0.98	7 ± 2 [9]	4.2[d]	0.67 ± 0.09
	dodecane	1.51	5 ± 1	3.1[e]	0.46
	hexadecane	3.34	1.9 ± 0.2	1.8[e]	0.45
PSA	water	1.00	3.7 ± 0.9 [2]	4.2[f]	12.8 ± 0.2
PDA	cyclohexane	0.98	6 ± 1 [2]	4.2[d]	2.4 ± 0.2
	2-propanol	2.5	0.9 ± 0.2	2.2[f]	0.74

[a] For more than single measurements the number of determinations are given in brackets. For single measurements the errors are related to values that lead to an increase of 10% in the value for the sum of the square of the residuals. Equal values were obtained for monomer or excimer decays for a particular experiment. The error limits do not incorporate the errors in the triplet concentrations (see text). [b] Calculated by the Smoluchowski equation taking spin statistics into account (see text). [c] Single measurements where errors are not indicated. Estimated error 10%. [d] The diffusion coefficient (7.2×10^{-6} cm^2 s^{-1}), obtained from Figure 4B in ref 22 for pyrene in linear hydrocarbons, was used for cyclohexane. [e] Diffusion coefficients from ref 22. [f] Extrapolated from $-\ln D$ vs $\ln (T/\eta)$ obtained for pyrene in hydrocarbons.[22]

of k_1. For this reason the emission intensities were maximized by using different gate sizes for different experiments. Equal values within the experimental error were obtained for $2k_{TTA}$ of pyrene in cyclohexane when the emission data were collected with a 120- or 1000-ns gate. Whereas the determination of k_1, a first-order constant, is independent of the conversion of observed signal into actual transient concentrations, the same is not true for $2k_{TTA}$. The uncertainty in the value for the initial triplet concentrations is incorporated in the error associated with $2k_{TTA}$. The magnitude of the overall errors increases in low-viscosity solvents, where the second-order TTA process is faster and therefore more triplets are depleted before data collection can begin. The TTA rate constants are close to diffusion limit when spin-statistics are taken into account (vide infra) and are thus dependent on solvent viscosity (Table I); the errors reported for single measurements are related to values for which a 10% increase is observed in the value for the sum of the square of the residuals. The same TTA rate constants are obtained when either the monomer or excimer decays are fitted to eq 5, as expected from the constancy of the E/M ratio.

The delayed fluorescence intensity for pyrene in acetonitrile is of the same order of magnitude as the one observed for the same pyrene concentration in hexane, solvents with similar viscosities. The excimer emission spectra in acetonitrile is red shifted by 15 nm in comparison to the one observed in hexane, as expected for higher polarity solvents.[23] The $(E/M)_{max}$ intensity ratios are similar in both solvents, and the $2k_{TTA}$ values are equal within the experimental error. In acetonitrile we also have detected the formation of the pyrene radical cation, probably as a result of a two-photon process (vide infra).

Chart I



Compound	Substituent	Abbreviation
Pyrene	none	
1-Dodecylpyrene	- $(CH_2)_{11}$-CH_3	DPY
1-Pyrenedodecanoic acid	- $(CH_2)_{11}$-COOH	PDA
4-Bromopyrene	- Br	BrPY
1-Pyrenesulfonic acid sodium salt	- SO_3^- ; Na^+	PSA
1,3,6,8-Pyrenetetrasulfonic acid sodium salt	- SO_3^-; Na^+	PTS

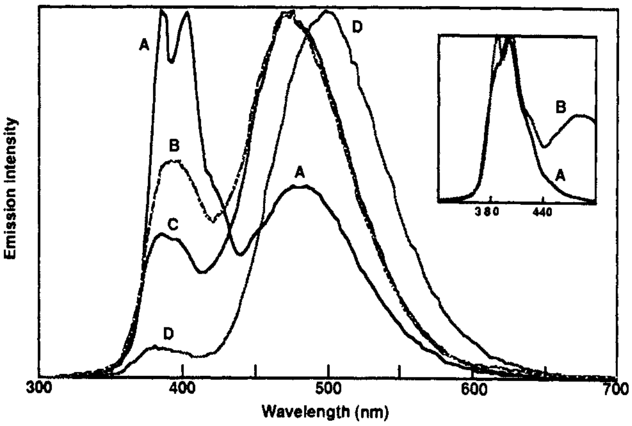


Figure 3. Delayed fluorescence of DPY (A) (50 µM, 10-µs delay, 600-ns gate), BrPY (B) (15-µs delay, 800-ns gate), and PDA (C) (30-µs delay, 600-ns gate) all in cyclohexane and PSA (D) (100 µM, 20-µs delay, 500-ns gate) in water. The insert shows the DPY prompt (A) and delayed (B) fluorescence.

The different pyrene derivatives studied are shown in Chart I. No excimer emission was observed in the prompt fluorescence of these molecules under the conditions employed. Delayed fluorescence was observed for all the pyrenes except PTS; the E/M intensity ratio is dependent on substitution (Figure 3, Table I). The monomer delayed fluorescence of DPY in cyclohexane shows small differences with the prompt emission (insert Figure 3), in contrast to the observation made with pyrene in the same solvent. Gas chromatographic analysis indicates that this effect is not due to pyrene or a related impurity in DPY. Until now we have been unable to find a reasonable explanation for this phenomenon.[24] For PDA in nonpolar solvents and for PSA the E/M ratio was too high to allow an accurate comparison of the detailed shape of the monomer contribution to the delayed and prompt emission spectra. The E/M intensity ratio was constant for delays that excluded prompt fluorescence and the contribution of the radical cation process (vide infra). For 4-bromopyrene (BrPY) the E/M ratio decreases slightly (~5%) after extensive laser irradiation, whereas for the other pyrenes no dependence with the irradiation dose was observed. The small increase in monomer emission for BrPY after extensive laser irradiation could be due to some loss of bromine and formation of pyrene. This debromination process,

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(23) *Excimers and Exciplexes*; Förster, T., *The Exciplex*; Gordon, Ware, Eds.; Academic Press, New York, 1975.

(24) One referee has suggested that this unusual effect may be due to "an enhancement of the forbidden 0–0 band induced by an interaction between an excited and an unexcited monomer in or near the solvent cage." This may indeed contribute, although we note that the excited monomer lifetime is much longer than the cage encounter.

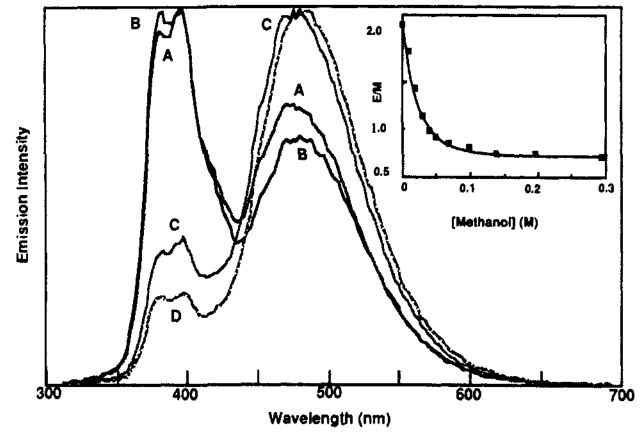

Figure 4. PDA delayed fluorescence (800-ns gate) in 2-propanol (A) (30-μs delay), acetonitrile (B) (17-μs delay), cyclohexane (C) (20-μs delay), and acetonitrile/water 1:1 (D) (15-μs delay). The emissions of (A) and (B) were normalized for the monomer intensity and the ones corresponding to (C) and (D) were normalized for the excimer. The insert shows the effect of methanol on the E/M ratio of PDA in cyclohexane. The $(E/M)_{max}$ at the plateau has a value of 0.80.

if it occurred, has to be quite inefficient as no change in the ground state absorption spectra, which could be ascribed to the presence of pyrene, was observed. Benzene was added in a 1:1 ratio to cyclohexane in an unsuccessful effort to detect the bromine-benzene complex in transient absorption experiments.[25]

No delayed fluorescence was observed for PTS in aqueous solution. The triplet of this molecule, monitored by its transient absorption spectra, is very long lived ($\tau_T > 700$ μs).[26] The lack of delayed fluorescence probably reflects the strong electrostatic repulsion that prevents encounters leading to TTA in this system. In support of this, we find that addition of high concentrations of NaCl (up to 1 M) shortens the triplet lifetime (~ 100 μs) and leads to detectable delayed fluorescence. At this high salt concentration the effective charge on the PTS molecule is decreased and repulsion is overcome.

The delayed fluorescence of PDA was studied in different solvents and a strong dependence of the E/M ratio was observed (Figure 4). Hydrogen-bonding solvents increase the monomer content. This was confirmed by the addition of methanol to PDA in cyclohexane (insert Figure 4). The E/M plateau value for PDA in cyclohexane at high methanol concentrations is similar to the E/M ratio obtained for DPY, which differs from PDA in the carboxylic group.

Figure 5 shows the triplet–triplet absorption spectra for different pyrene derivatives. All the absorption maxima were in the 415–430-nm region. The extinction coefficients, needed for eq 5, were estimated in the following manner: PTS has a triplet absorption that is slightly red-shifted with respect to pyrene and has a short fluorescence lifetime (12 ns, $\Phi_F = 0.47$). These features made it possible to determine the values of ϵ at 425 nm by using Aberchrome-540 as an actinometer.[27] The laser power had to be attenuated with neutral density filters to avoid ground-state depletion of PTS. From the Aberchrome method the product $\Phi_{isc}\epsilon$ obtained at 425 nm was 10300 ± 900 M^{-1} cm^{-1}. If we assume that ($\Phi_F + \Phi_{isc}$) is unity, then the Φ_{isc} value is 0.53 and consequently ϵ is 19400 ± 1700 M^{-1} cm^{-1}. For the other pyrenes it was not possible to determine ϵ, and a value of 25000 M^{-1} cm^{-1} obtained as the average between PTS and pyrene was used to estimate the initial triplet concentrations. In fact, it is very unlikely that any of these pyrene molecules will not fit within the range defined by pyrene and PTS, as all the triplet–triplet absorption spectra are similar. Thus, at most an error of about 25% is incorporated in the determination of the values of $2k_{TTA}$ for the different pyrene derivatives.

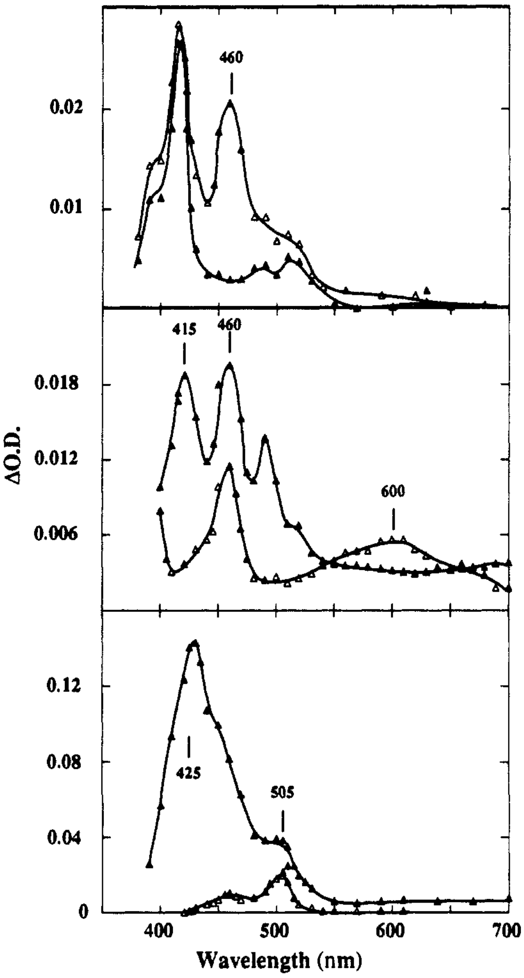

Figure 5. Top: PDA transient absorption spectra in cyclohexane (▲) and acetonitrile (△) 3 μs after the laser pulse. Middle: PSA (50 μM) transient absorption spectra in water in the absence (▲) and presence (△) of methyl viologen (4 mM). Bottom: PTS (100 μM) transient absorption spectra in water in the absence (▲) and presence (△) of oxygen respectively at 2 and 3 μs after the laser pulse.

The $2k_{TTA}$ values for PSA in water and PDA in cyclohexane and 2-propanol approach the diffusion-controlled limit when spin statistics are taken into account (Table I) (vide infra). Thus, ring substitution on pyrene and the very different interactions of pyrene derivatives in the triplet–triplet encounter complex, as evidenced by the different E/M delayed fluorescence intensity ratios, do not affect the observed dynamics for the TTA process. Again, the $2k_{TTA}$ values are the same for the monomer and excimer decays.

The use of polar solvents mentioned above brings us to an important aspects of the photolysis of pyrenes in this media. While laser photolysis in cyclohexane and other nonpolar solvents leads only to excited states, in the case of acetonitrile and hydroxylic solvents we find that radical-ion formation is a common process. This is known to be at least in part due to a two-photon process.[28,29] For PSA and PDA the radical cation is observed at 460 nm and for PTS this species absorbs at 460 and 505 nm (Figure 5). In the case of PSA the assignment of the 460-nm band to the radical cation was confirmed by the lack of oxygen quenching and by its presence when PSA triplet (λ_{max} 415 and 500 nm) was quenched by methyl viologen, which leads to the concurrent formation of the radical cations from PSA and methyl viologen (Figure 5).[30]

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(25) McGimpsey, W. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2299–2301.

(26) A very fast low intensity emission, with high monomer content, is detected. As this emission is much shorter than the triplet lifetime it cannot be ascribed to the TTA process.

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Table II. Monomer Fluorescence Quantum Yields and Singlet Lifetimes for the Different Pyrene Derivatives

substrate	solvent	τ_f,[a] ns	ϕ_m
pyrene	cyclohexane	420 ± 20	0.65[b]
DPY	cyclohexane	212 ± 8	0.89 ± 0.06
PDA	isooctane	260	0.54 ± 0.01
BrPY	cyclohexane	2.32 ± 0.03[c]	0.050 ± 0.004
PSA	water	64	0.71 ± 0.02
PTS	water	12	0.47 ± 0.01

[a] Single measurements where errors are not indicated. Estimated error 5%. [b] Taken from ref 19. [c] A slow decay with a 2% contribution to the intensity is observed. The value indicated corresponds to the fast decay.

For PSA in water an initial fast decay (3.0-μs lifetime measured at 460 nm) assigned to the radical cation is observed. The PTS transient absorption spectra (Figure 5) is broad due to the spectral overlap of the triplet and the radical cation. In the presence of oxygen only the absorption of the radical cation is observed at 460 and 505 nm. The possibility that the 505-nm band could be due to the radical anion produced via electron trapping was ruled out as it persists in the presence of N_2O, a hydrated electron trap.[31] We note that the radical cation does not absorb significantly at 425 nm, the wavelength where the triplet molar absorptivity was determined.

For pyrene molecules which showed the formation of radical cations, an additional emission was observed after the prompt fluorescence decay. The E/M ratio increased between 3.0-μs (end of the prompt fluorescence decay) and 15–20-μs delays, being constant thereafter. This indicates that some process involving the radical cation contributes to the monomeric emission, thus decreasing the E/M ratio at short delays. The initially higher monomer emission has a lifetime similar (3.0 μs for PSA in water) to the one observed for the decay of the 460-nm absorption assigned to the radical cation. All the studies related to the TTA process (i.e. the determination of the $2k_{TTA}$ values) were performed after the decay of the emission attributed to the radical cation.

The monomer fluorescence quantum yield of the different pyrenes under the deaeration conditions of the laser experiments was obtained by using as a standard the value of 0.65 for pyrene in cyclohexane.[19] These values and the respective monomer lifetimes are shown in Table II.

Discussion

The study of P-type delayed fluorescence in pyrenes employing modern techniques, based on laser excitation and gated OMA detection, offers two major advantages over earlier work that employed low power (i.e. lamp) excitation sources:[4–6,8,10] (i) The use of low ground-state concentrations results in no excimeric emission in the prompt fluorescence and (ii) the TTA rate constant can be obtained from the emission decay, which at high excitation doses shows a major contribution due to second-order processes. In contrast, in earlier work, when TTA was a minor perturbation on a dominant first-order decay, no information on the value of $2k_{TTA}$ could be obtained. The values of $2k_{TTA}$ determined here are a measure for the rate of triplet disappearance and do not incorporate the efficiency of formation for the emitting species. The fact that the TTA rate is close to the diffusion limit (and thus is controlled by solvent viscosity) makes this process convenient for the study of mobility characteristics of different systems, such as micellar collisions or protein interactions.[32]

The maximum rate of triplet removal in the annihilation process corresponds to $^5/_9$ of the triplet encounters, which account for the singlet and triplet encounters,[33] as quintet encounters are dissociative on energetic grounds. The diffusion-controlled rate for equal molecules is one-half of the one defined by the Smoluchovski equation.[34] Thus, the diffusion limit for $2k_{TTA}$ is given by

$$2k_{TTA} = {}^5/_9(4\pi N'RD) \qquad (6)$$

where N' is the Avogadro number in mM^{-1}, R is the sum of the radii ($2 \times 3.5 \times 10^{-8}$ cm), and D is the sum of the diffusion coefficients of the molecules involved in the collision. The calculated values of $2k_{TTA}$ based on a diffusion model are shown in Table I and agree within a factor of 2 with the experimental ones. We note that the diffusion coefficients are those for pyrene in hydrocarbons and that the values for PSA and PDA may be somewhat smaller.

The values for $2k_{TTA}$ show that taking spin-statistics into account the TTA process is diffusion controlled. Note that $2k_{TTA}$ values are equal (within the experimental error) to the rate constants for excimer formation ($6.7 \times 10^9\ M^{-1}\ s^{-1}$).[35] The latter process does not have spin restrictions and could be higher than $2k_{TTA}$ by a factor of 1.8, thus suggesting that the rate for excimer formation could be somewhat smaller than the diffusion limit. We note that if the rate for excimer formation was diffusion controlled all the TTA encounter complexes should initially lead to excimers. We would therefore expect a higher E/M at high viscosity; this does not appear to be the case (see Table I).

The excimer content of the delayed fluorescence is dependent on the pyrene substitution. This difference cannot be accounted for by changes in the monomer and excimer emission quantum yields. The E/M ratios for PSA and pyrene differ by a factor of almost 20 (Table I), but their monomer emission quantum yields are very close (0.71 and 0.65, respectively) (Tables I and II). The pyrene excimer emission quantum yield is 0.75,[19] and if the differences between the E/M ratios were due only to the increase of the PSA excimer emission quantum yield this value would be much higher than 1.0. Thus, the differences in E/M must be a true reflection of variations in the yields for monomer and excimer formation.

The higher excimer contribution in the delayed fluorescence for PSA, PDA, and BrPY relative to pyrene must be related to the mechanism of excimer formation in the triplet–triplet encounter complex. We feel that the exclusive formation of monomers in this encounter complex, with excimers being formed via the reencounter of the monomer with the ground-state annihilation partner, is improbable. As the emission lifetimes of the monomers and excimers are much longer than the lifetime of the solvent cage, the E/M ratio in the case of monomer-only formation would depend only on the solvent cage lifetime and the E/M ratio should be similar for different pyrenes in the same solvent. The higher excimer contribution for the substituted pyrenes is probably related to an intrinsic increased yield of excimer formation (pathway 1 in Scheme I) in the TTA process, to a faster geminate association to yield excimer (pathway 3) or to a slower dissociation (pathway −3). Currently we cannot differentiate between these possibilities. It is important to note that the direct excimer formation is consistent with the idea that TTA can only occur at very short distances as no delayed fluorescence was observed for PTS, suggesting that a long-range process is probably not efficient at room temperature.

The E/M intensity ratio of the pyrene derivatives depends not only on the nature of the substituent, but for some molecules, like PDA, it shows a remarkably large dependence on the solvent used. It is important to note that pyrenes that do not contain groups prone for solvent interaction do not show a significant change in the E/M ratio in going from hexane to acetonitrile. We believe that the solvent dependence of the PDA delayed fluorescence reflects that in nonpolar solvents, such as cyclohexane, the association of the carboxylic acid groups (which is well-known in simple systems such as CH_3COOH)[36] assists excimer formation during the triplet–triplet encounter. The monomer content of the delayed emission is increased with the addition of methanol to PDA in cyclohexane, presumably as a result of its favorable competition

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(31) Janata, E.; Schuler, R. H. *J. Phys. Chem.* **1982**, *86*, 2078–2084.

(32) Preliminary results with AOT/water/isooctane reversed micelles obtained in our labortories indicate the usefulness of this approach.

(33) Two triplets are removed in the singlet encounter.

(34) Saltiel, J.; Atwater, B. W. *Adv. Photochem.* **1988**, *14*, 1–90.

(35) Birks, J. B.; Lume, M. D.; Munro, I. H. *Proc. R. Soc.* (*London*) **1964**, *280A*, 289–297.

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for association with the carboxylic group. The same effect can be achieved by use of good hydrogen bonding molecules, such as neat acetonitrile or 2-propanol as solvent (Figure 4). Effectively, carboxylic association leads to a longer lived encounter than it would be otherwise. Interestingly, in water–acetonitrile the E/M ratio increases. This cannot be attributed to ground-state aggregation of PDA as no excimer emission was observed in the prompt fluorescence. We tentatively attribute this phenomenon to hydrophobic association of PDA molecules following the TTA encounter.[37] The separation of two PDA molecules is expected to be entropically unfavorable in water–acetonitrile as more solvent molecules would have to be organized around the hydrophobic solute molecules. Thus, a higher solvent reorganization free energy would be associated with the separation of PDA molecules in aqueous solvents.

PDA could conceivably form dimers in the ground state in nonpolar solvents. The end-to-end cyclization of these dimers would have to be slow as no excimers are observed in the prompt fluorescence. Further, one would also expect that the E/M ratio of the TTA process involving the interaction of triplet dimers with monomers or dimers would be different from the E/M for "free", monomeric PDA triplets. The consequence would be that this ratio should vary over time. The E/M ratio was constant over the measured time range. Thus, "intramolecular" (in the dimer) TTA does not contribute to the delayed fluorescence in our case.

Finally, the characterization of the delayed fluorescence of pyrenes in homogeneous solution opens different possibilities in the use of these molecules as probes for mobility. The probing by delayed fluorescence should offer in some cases enhanced and unique opportunities over the prompt fluorescence: enhanced in that the time window for reporting relates to the much longer triplet, rather than singlet lifetime; unique in that under carefully selected conditions (i.e. no prompt excimer emission and exclusion of the radical cation process) the excimer delayed luminescence is an unequivocal test for the encounter of probe molecules and thus of mobility. Further work is clearly needed to address in detail the relative importance of the pathways in Scheme I. This will be subject of future work.

Experimental Section

Pyrene from Princeton Organics and methyl viologen (Aldrich) were recrystallized from ethanol and *p*-methoxyacetophenone was recrystallized from ethanol–water. 1-Dodecylpyrene (DPY), 1-pyrenedodecanoic acid (PDA), 1-pyrenesulfonate (sodium salt, PSA) and 1,3,6,9-pyrenetetrasulfonate (sodium salt, PTS) from Molecular Probes, 4-bromopyrene (BrPY), methanol, and cyclohexane from Aldrich, hexane, dodecane, and sodium hydroxide from J. T. Baker Chemical Co., acetonitrile from Omnisolv, 2-propanol from Fisher Scientific, and Aberchrome-540 from Aberchromics Ltd. were used as received. The purity of DPY was checked by gas chromatography. Hexadecane from BDH was stirred overnight with 1:1 H_2SO_4–HNO_3 (5:1 hydrocarbon–acid mixture). The organic phase was washed with water, with sodium bicarbonate, and again with water. Hexadecane was distilled at reduced pressure. The conductivity water was purified by a Milli-Q Water Purification system.

Steady-state fluorescence measurements were performed on a Perkin-Elmer LS-5 spectrofluorimeter supported by a PE-3600 data station, and lifetimes were obtained with PRA single photon counting equipment with a hydrogen lamp as the excitation source or with a Gregg Phase Shift Spectrofluorimeter where phase and modulation lifetimes gave a single value when the excitation frequency was changed from 3 to 6 MHz. Absorption spectra were measured on a HP-8451A diode array spectrophotometer.

The laser system at NRC has been described earlier.[38,39] Kinetic absorption data were acquired with an RCA-4840 photomultiplier for detection and luminescence data with an EG&G gated and intensified optical multichannel analyzer (OMA).[40,41] The delay after the laser pulse can be adjusted in the OMA gate in 10-ns steps up to 1 ms, whereas the gate for data collection is either fixed at 20 ns or adjusted in 10-ns increments from 120 ns to 1 ms, although the longest gate employed was only 1 μs.

Samples of pyrene, DPY, BrPY, PSA, and PTS were prepared from stock solutions of known concentrations. PDA stock solutions in hexane or methanol were cloudy even after extensive sonication and were passed through Millipore filters. Only stock solutions with low concentrations were obtained, and to solubilize PDA in different media a film was prepared in a flask by evaporating the hexane or methanol with nitrogen. After the solvent to be used in the experiment was added, the solutions were sonicated for 2 h and were then transferred to the cell to be used in the laser experiments. All the samples were excited with a Molectron UV-24 laser at 337.1 nm (~8 ns, ≤4 mJ/pulse) employing a front-face geometry to avoid the effects of reabsorption of the emission. The concentration of the pyrenes for laser experiments was such as to obtain absorbances between 0.1 and 0.6[42] at 337 nm for a 3-mm optical path.

All samples were deaerated for 15 min by nitrogen bubbling, and the experiments were performed in 3 × 7 mm² cells in the laser experiments and in 10 × 10 mm² cells for steady-state fluorescence and single photon counting measurements. Occasionally some minor changes of the ground state absorption spectra were observed following laser excitation; when this was the case, the sample was shaken in between irradiation cycles (each cycle consists of 20 laser pulses). This was sufficient to offset this minor effect, and use of a flow system was not required.

A computer program was used to obtain $2k_{TTA}$ values by fitting the experimental data to eq 5. The initial triplet concentrations were obtained from absorption measurements and value ranges were set for k_1, α, and k_{TTA}. Different steps (up to 20) were chosen for each parameter, and the program searched for the combination of values with lowest sum of the square of the residuals. The computer then sets new ranges and repeats the procedure until the difference between two subsequent values of the sum of the square of the residuals is below 0.5%.

The initial triplet concentration ($[T]_0$) was obtained from absorbance measurements at the OMA. The true optical path in a 3 × 7 mm² cell under the experimental conditions used (laser alignment and optical density at the laser wavelength) had to be determined because the laser cell is irradiated by the N_2 laser from the front at a ~20° angle with respect to the monitoring beam. The true optical path was estimated by measuring the absorption of triplet *p*-methoxyacetophenone[21] in cyclohexane in cells with 0.3, 0.7, and 3.0 mm pathlength. By correlating the signal intensity to the optical path the true pathlength in a 3 × 7 mm² cell was determined to be 2.3 ± 0.3 mm. The difference between 2.3 and 3 mm optical path reflects an inefficiency in the excitation resulting from the angle of incidence of the laser beam.

The triplet absorption of pyrene cannot be measured at short delays due to interference of prompt fluorescence. The triplet–triplet absorption was typically measured 3.0 μs after the laser pulse and was extrapolated to zero time with use of the parameters of a curve fit when the initial triplet concentration was set to be somewhat higher than the one determined at 3.0 μs. The correction due to this extrapolation was typically 20%.

Our analysis assumes that the gate size is small enough to allow a true sampling of the decay curve; i.e. TTA is much slower than the other processes (monomer and excimer decay) leading to emission. No effect on the dynamics or E/M was observed when the detection gate was changed between 120 and 1000 ns.

The monomer fluorescence quantum yields for the different pyrene derivatives were determined as described by Demas and Crosby,[43] using as a reference the value of 0.65 for pyrene in cyclohexane.[19] The absorbance at the excitation wavelength was maintained below 0.06, and appropriate corrections for solvent refractive indexes were introduced.

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