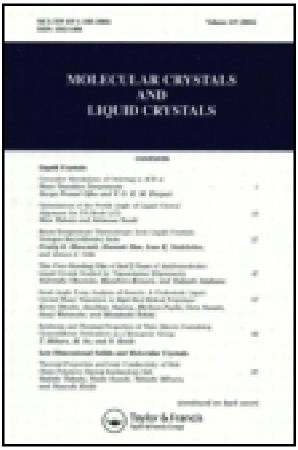

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Laser-Excited Delayed Fluorescence of Crystalline *p*-Terphenyl

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The steady state and time-dependent laser excited delayed fluorescence from high purity *p*-terphenyl single crystals is discussed. Both are shown to be highly dependent on the presence of deep trapping centers at a concentration $\leq 10^{-8}$ mole/mole. General equations for the decay of the host delayed fluorescence in the presence of traps under conditions of weak excitation directly into the triplet state are employed to yield the trapping parameters. In addition the study of delayed fluorescence spectra and the total intensity of delayed fluorescence with temperature yields information about singlet and triplet exciton localization by the traps. ΔE_1^S and ΔE_1^T, the singlet and triplet trap depths respectively, are 4,600 ± 100 cm^{-1} and 7,550 ± 500 cm^{-1} and at 190 K, β_p the trap decay rate is 44 ± 6 s^{-1}. These values are consistent with trapping centers formed by the substitution of anthracene molecules in the *p*-terphenyl lattice. The reported phase transition in *p*-terphenyl at *ca* 190 K has no marked effect on the triplet trapping behavior.

INTRODUCTION

Excitonic investigations involving both doped and "pure" molecular crystals together with structural studies provide conclusive evidence that chemical and structural defects act as both singlet and triplet exciton traps.[1,2] As even most of the highly purified molecular solids, notably anthracene and tetracene, contain traps the question arises whether those of chemical or structural origin are dominant. Indeed these two materials have been studied extensively in this context over the past decade and we have a reasonable understanding of the behavior of both singlet and triplet excitons and the role of trapping centers.

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Interest in *p*-terphenyl single crystals has not been so intense to date despite the fact that this material in its high temperature modification has a similar crystal structure to both anthracene and tetracene, can be highly purified and grown as suitably large single crystals, and has lower excited singlet and triplet energy levels accessible to selective excitation by visible laser radiation. *p*-Terphenyl has the added attractive feature of a phase transition at *ca* 190 K that converts the high temperature monoclinic form to a low temperature triclinic phase. Several investigations have been carried out across this phase transition following its structural characterization by X-ray[3] and neutron diffraction[4] and electron microscopy combined with lattice energy calculations.[5,6] These include measurements of charge-carrier mobilities,[7] Raman spectra,[8] fluorescence spectra[9] and lifetimes[10] and absorption spectra[11,12] and have contributed appreciably to our understanding of this solid. Studies involving triplet excitons are, however, very few; a notable exception is the study of Funfschilling *et al.*[13] of the magnetic field dependence of the delayed fluorescence between 130 K and 300 K. This study demonstrated that shallow triplet traps resulting from slightly perturbed *p*-terphenyl molecules introduced into the more regular structure in the region of the phase transition affect the magnetic field dependence of the delayed fluorescence. A simple model was proposed in which the spin relaxation in these shallow traps is magnetic field dependent, and differs from that of the free exciton. No discontinuity in the carrier mobility/temperature dependence has been observed across the phase transition but the hole and electron photocurrent transients at all temperatures are controlled by thermal detrapping processes.[7] As part of a program to investigate crystalline *p*-terphenyl we have adopted an approach, developed earlier for the study of anthracene,[1,14] that allows us to investigate in some detail the triplet exciton dynamics using both steady-state and temporal dependences of delayed fluorescence (and phosphorescence) as a function of temperature. This allows us to elucidate the trapping properties in a temperature range for *p*-terphenyl that includes the phase transition.

GENERAL CONSIDERATIONS

Steady-state delayed fluorescence

The total intensity of delayed fluorescence I_{DF} for weak excitation may be expressed as

$$I_{DF} = \frac{1}{2} \gamma n \left(n + \sum_i c_i n_i\right) \qquad (1)$$

where γ is the bimolecular annihilation rate constant for free-free triplet interactions, n is the concentration of free triplets, n_i is the concentration of triplets trapped in levels signified by the subscript i and γc_i is the rate constant for free-trapped triplet annihilation leading to delayed fluorescence. It is assumed that the factors c_i are in the main different from unity. For a host-guest system either host or guest emission may occur as a result of free-trapped triplet annihilation. Under photo-stationary conditions the expression for the total intensity of delayed fluorescence may be written as[14,15]

$$I_{DF} = \frac{1}{2}\gamma\left(\frac{\alpha I}{\beta}\right)^2 \frac{1+\sum_i c_i A_i}{\left(1+\sum_i \frac{\beta_i}{\beta} A_i\right)^2} \equiv \frac{1}{2}\gamma\left(\frac{\alpha I}{\beta}\right)^2 B \tag{2}$$

where α is the $S_0 \rightarrow T_i$ absorption coefficient, I is the intensity of exciting light, β and β_i are the unimolecular decay constants for free and trapped triplets, i.e. τ_x^{-1} and τ_p^{-1} respectively (see Figure 1). $A_i \equiv p_i/(\beta_i + q_i)$ with p_i the trapping

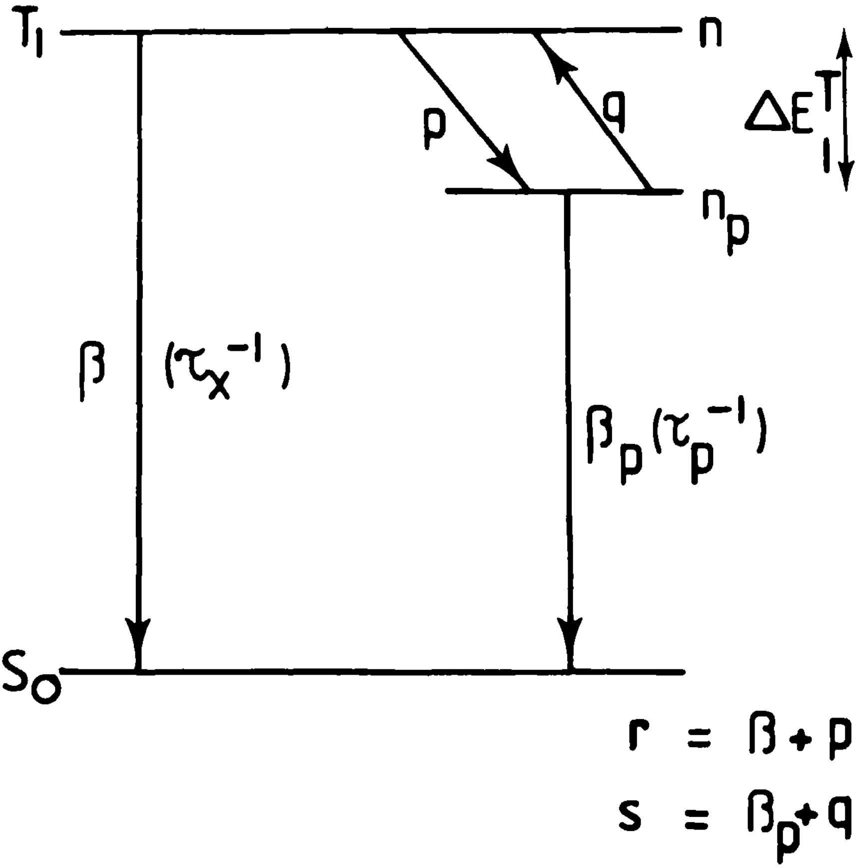


FIGURE 1 Energy levels and rate constants as used in the text.

rate constant for the ith trap equal to Z_iN_i where Z_i is the collision rate between free excitons and traps of type i and concentration N_i; q_i the release rate from a trap of depth ΔE_i; $q_i = Z_iN \exp(-\Delta E^T_i/kT)$, N is the concentration of host molecules in the crystal. In the case of traps well separated in energy I_{DF} will generally decrease upon lowering the temperature reflecting the decrease in concentration of the free triplets caused by trapping.

Translent behavlor—hlgh temperature

With weak excitation where all bimolecular effects may be neglected and with one trapping level denoted by p (see Figure 1)

$$\frac{dn}{dt} = \alpha I - \beta n - pn + qn_p = \alpha I - rn + qn_p \tag{3}$$

$$\frac{dn_p}{dt} = -\beta_p n_p - qn_p + pn = -sn_p + pn \tag{4}$$

where n_p is now the trapped triplet density.

Eliminating n_p we get

$$\frac{d^2n}{dt^2} + (r+s)\frac{dn}{dt} + (rs - pq)n = 0 \tag{5}$$

whose solutions have the general form

$$n = a \exp(-\lambda t) + b \exp(-\mu t) \tag{6}$$

subject to the initial conditions $n(0) = n_0(I)$ and $n_p(0) = 0$, i.e. direct population of the triplet traps by laser photons is neglected. From Eq. (3) the latter condition is equivalent to $dn/dt_{t=0} = -rn_0$. Hence the relationships[16]

$$\lambda = \left[\left(\frac{a}{b}\right)r - s\right] \Big/ \left[\left(\frac{a}{b}\right) - 1\right] \tag{7}$$

and

$$\mu = \left[\left(\frac{a}{b}\right)s - r\right] \Big/ \left[\left(\frac{a}{b}\right) - 1\right] \tag{8}$$

In the simple case where $a/b \gg 1$, $\lambda \simeq r$ and $\mu \simeq s$; that is the initial decay is that of the free triplet by deactivation and trapping, and the long time decay is that of the trapped triplet. If $a/b \simeq 1$ then

$$r = \frac{\frac{a}{b}\lambda + \mu}{\frac{a}{b} + 1}, \quad s = \frac{\frac{a}{b}\mu + \lambda}{\frac{a}{b} + 1}, \quad pq = \frac{\frac{a}{b}(\lambda - \mu)^2}{\left(\frac{a}{b} + 1\right)^2} \tag{9}$$

must be employed.

Transient behavior—low temperature

For the situation of a dominant, deep triplet trap then as the temperature is lowered the effect of this trap on the delayed fluorescence wave-form by a lowering of the rate of depopulation, will become more apparent. The kinetics are then best described by a model developed by Ern.[17] Under such conditions the build-up $I^b_{DF}(t)$ and decay $I^b_{DF}(t)$ of the delayed fluorescence wave-form following square wave excitation directly into the free triplet state will be described by

$$I^b_{DF}(t) = K\,\{[1 - \exp(-rt)]\,[1 - \exp(-\beta^1 t)] + \rho\,[1 - \exp(-\beta^1 t)]^2\} \quad (10)$$

$$I^d_{DF}(t) = K\,\{\exp(-rt) + \rho\,\exp(-2\beta^1 t)\} \quad (11)$$

where K is a constant,

$$\rho = pq(\beta_p r + \beta q)^{-1} \quad (12)$$

and

$$\beta^1 = \beta_p + (\beta/r)q \quad (13)$$

The delayed fluorescence signal is entirely due to free-trapped triplet exciton annihilation since the concentration of free triplets is smaller than the trapped population. There is strong asymmetry in the behavior of the build-up and decay portions of the wave-form. The build-up is usually slow having two components with temporal behaviors $[1 - \exp(-\beta^1 t)]$ and $[1 - \exp(-\beta^1 t)]^2$. The last of these is the same as for mutual annihilation of free excitons with a hypothetical decay rate β^1. Since $r/\beta^1 \gg 1$ the coefficient of $[1 - \exp(-\beta^1 t)]$ is unity on the time scale of the wave-form and the proportion of the two components is given by ρ. The decay portion of the wave-form shows two components also given in the proportion ρ. The fast component $\exp(-rt)$ appears to follow the shut-off of the exciting light on the time scale of the observations while the slow component has a decay time given by $2\beta^1$. At low temperatures ($1/\beta^1$ approaches τ_p the lifetime of the trapped triplets. If r and β have similar orders of magnitude Eq. (12) predicts that ρ, the relative ratio of the slow to the fast component in the wave-form, will increase with temperature to a finite value given by $p\beta$ i.e. to a value given by the ratio of the trapping to the direct decay rates of the free triplets. At low temperatures ρ becomes proportional to q and should decrease with decreasing temperature as $\exp(-\Delta E^T_1/kT)$.

In studying the delayed fluorescence wave-form the exciting light has a square-wave modulation with period T so that $i = i_0$ for $0 \leq t \leq T/2$ and $i = 0$ for $T/2 \leq t \leq T$. Normally the frequency of modulation ω is chosen to be sufficiently small with respect to the smaller of the two relevant rates, r and s, ω/r, $\omega/s \ll 1$. Variation of ω, however, can yield important supplementary information.[17] If $\omega \simeq \beta$ and $\omega \ll r$ the low frequency wave form developes an initial "step" also in the build-up region since now some trapped population is still present at the beginning of the "on" cycle. The relative proportion of this "step" in the wave-form grows with increasing frequency.

EXPERIMENTAL

Material purification and crystal preparation

Commercially available *p*-terphenyl (Koch-Light Ltd) was chromatographed on aluminia and silica-gel columns employing ethanol as elutrient under inert conditions in the dark. The product was vacuum sublimed and zone-refined for *ca* 100 passes. The material was then transferred to a combination tube (zone refining and crystal growth sections) zone refined under vacuum and transferred without exposure to air to crystal growth ampules. Crystals were generally grown from the vapor phase[1,18] to yield bulky crystals (ingots) *ca* 2 cm long and 1 cm diameter. (001) faces were prepared by cleavage.

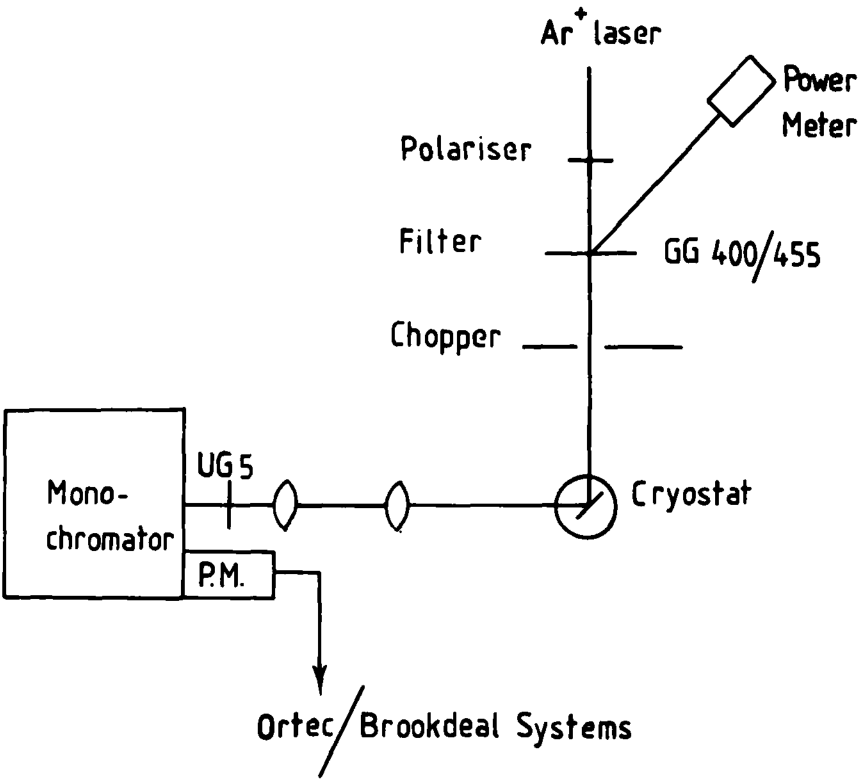


FIGURE 2 Schematic diagram of the experimental arrangement.

Measurement of steady state and time-dependent delayed fluorescence

A schematic diagram of the experimental arrangement is shown in Figure 2. The excitation source was and Ar^+ ion laser operating at 457.9 nm with *ca* 5 mW CW power (Spectra Physics Model 171). The light travelled through a polarizer (to vary the excitation intensity) and a filter (GG400 or GG455 cut-off filters at 400 nm and 455 nm respectively) before impinging on the rotating blades of a light chopper (Ortec Brookdeal Model 9479). The blue light excited delayed fluorescence directly in a crystal freely mounted in an optical cryostat (Oxford Instruments CF 100). The emitted delayed fluorescence in the temperature range 77 K to 305 K was observed at 90° by a cooled photomultiplier (RCA 8850) through a uv transmitting filter (UG5) and a double monochromator (Hilger D330/331). The signal was detected either by a photon counter (Brookdeal C51) and displayed on a chart recorder (spectral measurements) or a multichannel analyzer-photon counting combination (transient measurements) (Inotech-Ortec) interfaced to a microcomputer (Research-Machines 380Z). Several thousands of sweeps at a chopper frequency ranging from 10–50 Hz and corresponding to 5000–10000 counts in the peak channels were stored over times ranging from 2–30 mins since signals were invariably weak (typical dark count for photomultiplier was $\geq$ 50 counts s^{-1}). The wave forms were collected at selected wavelengths covering the delayed fluorescence spectrum and also with wide slit-widths so as to allow most of the delayed fluorescence intensity to pass for detection. Prompt fluorescence spectra and lifetimes were available from parallel studies.[10] The delayed fluorescence transients were fitted to exponential functions of the form described by Eqs. (10) and (11) employing a method of least squares. Lifetimes are obtained to an accuracy of 0.5 ms and are repeatable to within 1 ms for different cleaved sections.

RESULTS AND DISCUSSION

Delayed fluorescence spectra

The laser flux incident on the crystal, I, varied from *ca* 5×10^{16} to 5×10^{17} photons/cm^2 s. In this range it was verified that under all conditions $I_{DF} \alpha I^2$ so that bimolecular triplet decay processes may be neglected. With an incident flux of 10^{17} photons/cm^2 s and assuming an absorption coefficient $\alpha(S_0 \rightarrow T_1)$ for *p*-terphenyl of 1×10^{-3} cm^{-1} *ca* 5×10^{11} cm^{-3} triplets are generated.

The delayed fluorescence spectrum was recorded over the temperature range 300 K–77 K and compared with the corresponding prompt fluorescence spectra over the wavelength range 330 nm to 440 nm. Typical spectra are shown in Figure 3. There are clearly two components to the delayed fluorescence spectrum at the higher temperatures. The maxima at 365 nm, 387 nm and 395 nm are attributed to the host *p*-terphenyl emission with the lower

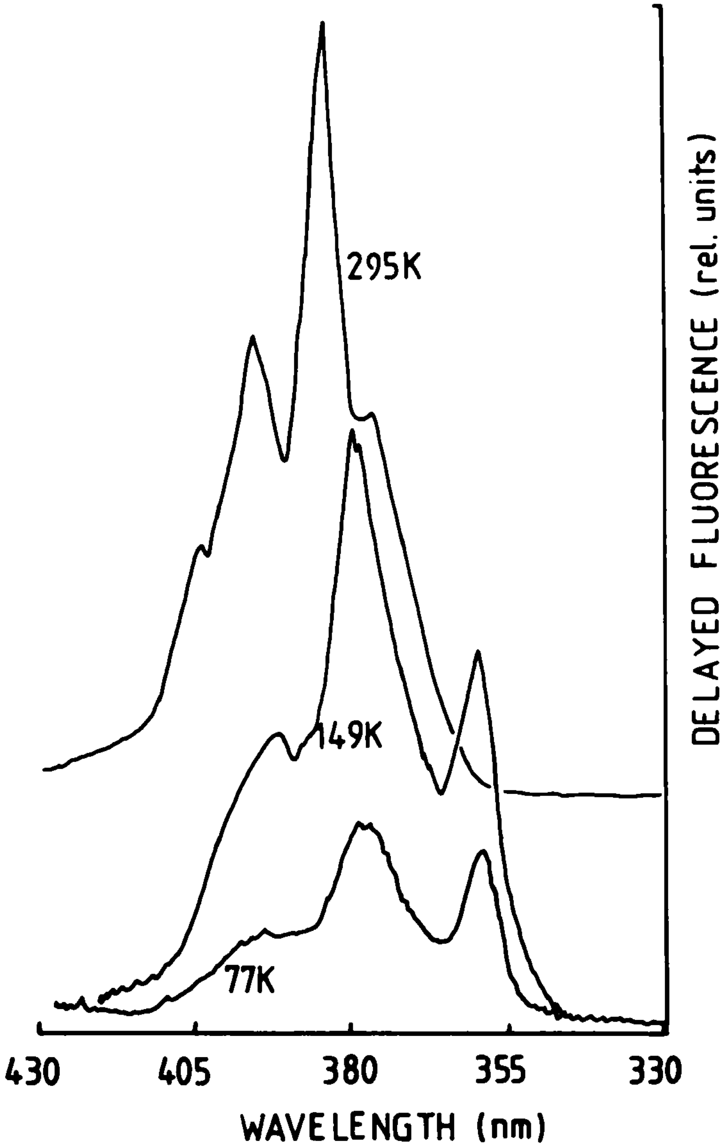
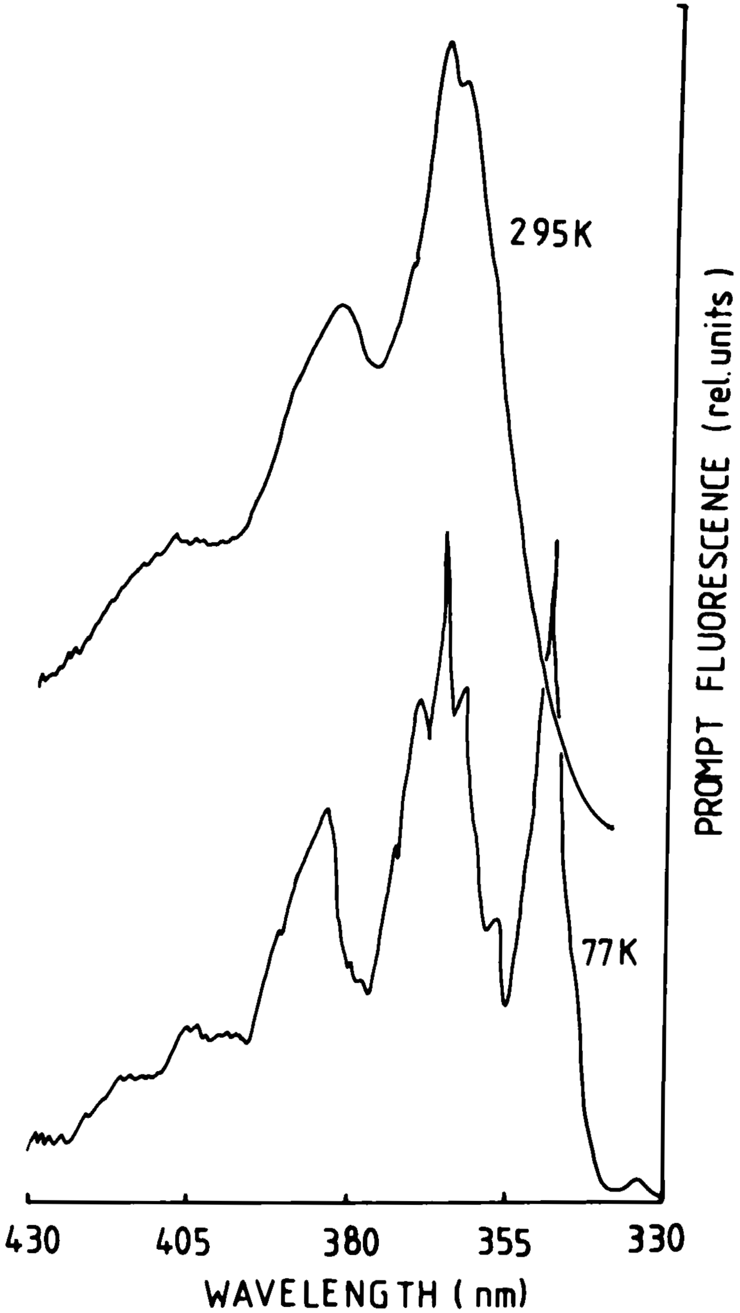


FIGURE 3 Delayed fluorescence spectra of *p*-terphenyl single crystal at various temperatures. A prompt fluorescence spectrum is also included for comparison.


295K
77K
PROMPT FLUORESCENCE (rel. units)
430
405
380
355
330
WAVELENGTH (nm)

wavelength maxima, observable in surface excited prompt fluorescence, now less apparent in delayed fluorescence because of reabsorption. An additional peak appears at 376 nm in high temperature spectra and disappears as the temperature is lowered. This emission is observed from both host and trap as a result of free-free and free-trapped triplet annihilations. A similar observation has been reported by Funfschilling and Zschokke-Granacher[19] for tetracene doped anthracene crystals and the sensitivity with which triplets can reveal traps as compared to singlets has been highlighted by Benz, Hacker and Wolf.[20] Our observations in delayed fluorescence and the fact that no such trapping may be observed in prompt fluorescence are in agreement with such considerations. If the peak at 376 nm represents the O—O of trap emission then taking the O—O of the crystalline *p*-terphenyl at 298 K as 31,200 cm^{-1} yields a singlet trap depth ΔE_1^S of *ca* 4,600 ± 100 cm^{-1}. Emission from trapped singlet disappears at low temperatures where free-free annihilation dominates over free-trapped triplet annihilation.

Temperature dependence of delayed fluorescence intensity (I_{DF}/T)

A typical I_{DF}/T dependence for a cleaved crystal under weak excitation is shown in Figure 4. This curve has not been corrected for fluorescence reabsorption since a detailed approach under our experimental conditions is not possible. However, we have shown elsewhere[10] that, at least in the temperature

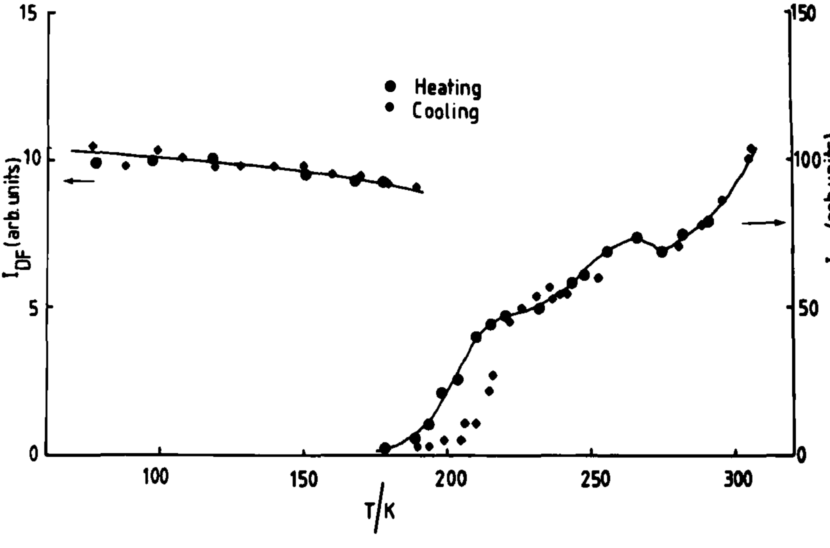


FIGURE 4 Temperature dependence of the delayed fluorescence intensity (I_{DF}) for a freshly cleaved *p*-terphenyl crystal.

range 77 K–200 K, reabsorption in *p*-terphenyl may be ignored. Between 200 and 300 K for *p*-terphenyl as for many other molecular crystals e.g. anthracene the correction is a slowly decreasing function with decreasing temperature and is unlikely to markedly affect our data. No quantitative information is obtained from the data included in Figure 4 but it clearly demonstrates the influence of trapping on I_{DF} (see Eq. 2). The trapping is pronounced even at 305 K and no drastic discontinuity is observed at the reported phase transition temperature of 190 K. However, below this temperature the decrease in I_{DF} is arrested and a slight increase is apparent with decreasing temperature down to 77 K. On warming the crystal, hysteresis sets in at *ca* 190 K but otherwise the I_{DF}/T dependence on repeated cooling and heating is reversible and representative of the crystalline material. The behavior is consistent with the presence of at least one deep trap for the triplets.

Temperature and frequency dependence of delayed fluorescence wave-forms

Despite the fact that delayed fluorescence wave forms have been recorded at two different wavelengths it is very difficult to isolate and quantify the emission from the host and guest. The decay parameters at 355 nm are likely, however to be more characteristic of the host *p*-terphenyl lattice and to contain a small amount of the trap emission whereas the decay parameters at 375 nm contain the trap emission and a large proportion of host emission. Our analysis will therefore be confined to the delayed fluorescence wave-forms recorded at 355 nm.

Typical delayed fluorescence transients are shown in Figure 5. The overall shape of the transients is independent of light intensity over the range investigated and there is no evidence of trap saturation effects as previously observed in the case of anthracene single crystals.[1] However, their shape is very dependent on the temperature of observation. Above 220 K the decay parts of the transient may be fitted to a sum of two exponential functions of the form given by Eq. (6). The corresponding decay rates are plotted against temperature in Figure 6. Although over the temperature range 220 K–305 K, λ and μ values for 355 nm appear different from those recorded at 375 nm a similar temperature dependence is observed—the faster decay rates falling off more rapidly with decreasing temperature than the slower ones. There is a sudden transition in the shape of the wave-form and in the temperature dependence of the decay rates as temperature is further lowered. The wave-forms take on the classical shape predicted by Ern[17] for the case in which a deep-triplet trap controls the kinetics of exciton annihilation. There is a sudden sharp decrease from the maximum value corresponding to this deep trapping followed by a slower decay. The ratio of the slow to the fast decay components ρ also increases as temperature increases. The slower decay component may be fitted to a single exponential function at all temperatures and for the two emission wavelengths

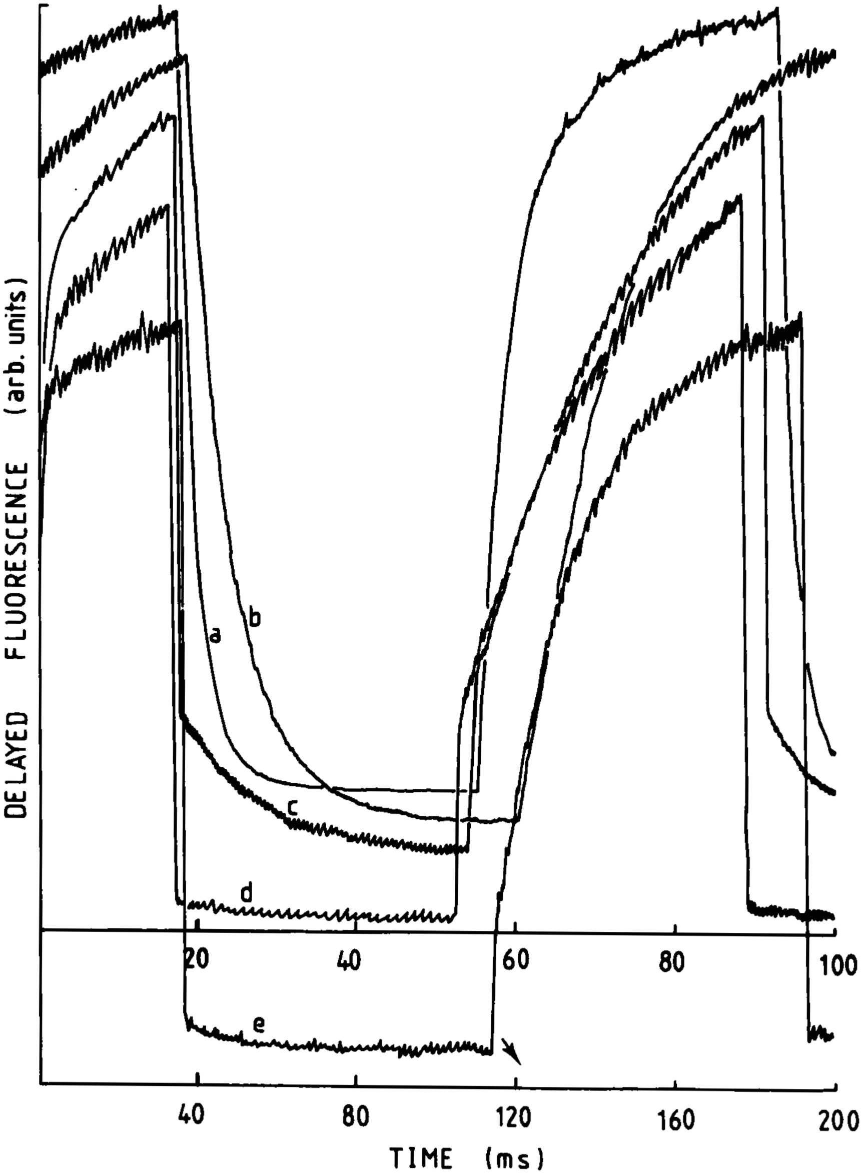


FIGURE 5 Typical delayed fluorescence wave-forms.

(a) $T = 263$ K; $\omega = 83s^{-1}$ (c) $T = 199$ K; $\omega = 83s^{-1}$

(b) $T = 248$ K; $\omega = 83s^{-1}$ (d) $T = 190$ K; $\omega = 83s^{-1}$

(e) $T = 190$ K; $\omega = 41s^{-1}$

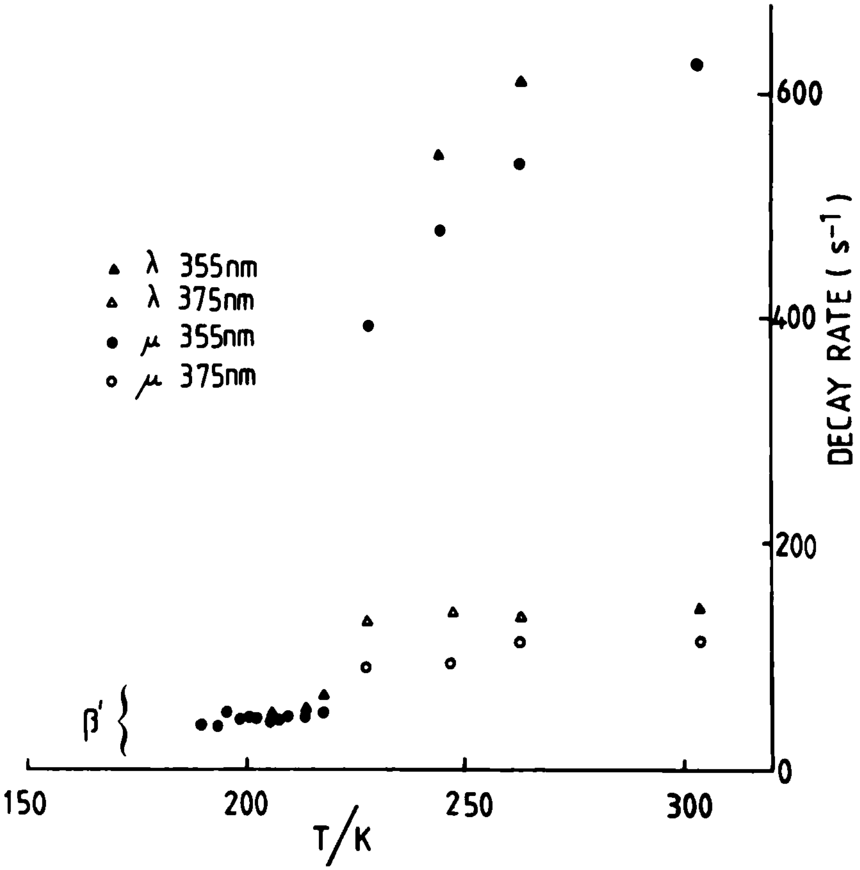


FIGURE 6 Temperature dependence of triplet decay rate λ, μ and β^1 for p-terphenyl.

in the temperature range 220 K–190 K. Below 190 K only the fast component is observed. The single exponential decay satisfies Eq. (11) with $r \gg 2\beta^1$ and since at the lowest temperature $\beta \ll \rho$ then $\beta^1 \approx \beta_p$ = constant, i.e. 44 ± 6s^{-1} (see Figure 6). ρ changes appreciably over a narrow temperature range yielding a value for ΔE_1^T of *ca* 7550 ± 500 cm^{-1} (see Figure 7). Thus the deep trap has the following characteristics; ΔE_1^T (triplet) = 7550 ± 500 cm^{-1}, β_p = 44 ± 6s^{-1} at 190 K and ΔE_1^s(singlet) = 4,600 ± 100 cm^{-1}. In the high temperatures regime where two decay times are observed then Eq. (6) is applicable and in our case a/b ranges between 1 and 5. At 304 K where $a/b = 1.13$; $r = 439\,(\pm\,50)\,s^{-1}$; $s = 414\,(\pm\,48)\,s^{-1}$; $pq = 4.03\,(\pm\,0.4) \times 10^4\,s^{-1}$. Although β, p, β_p and q cannot be obtained separately their values can be bracketed using the above values of r, s and pq, i.e. they all have values in the range *ca* 1 to $3 \times 10^2\,s^{-1}$. Thus both the free and trapped triplet concentrations are de-

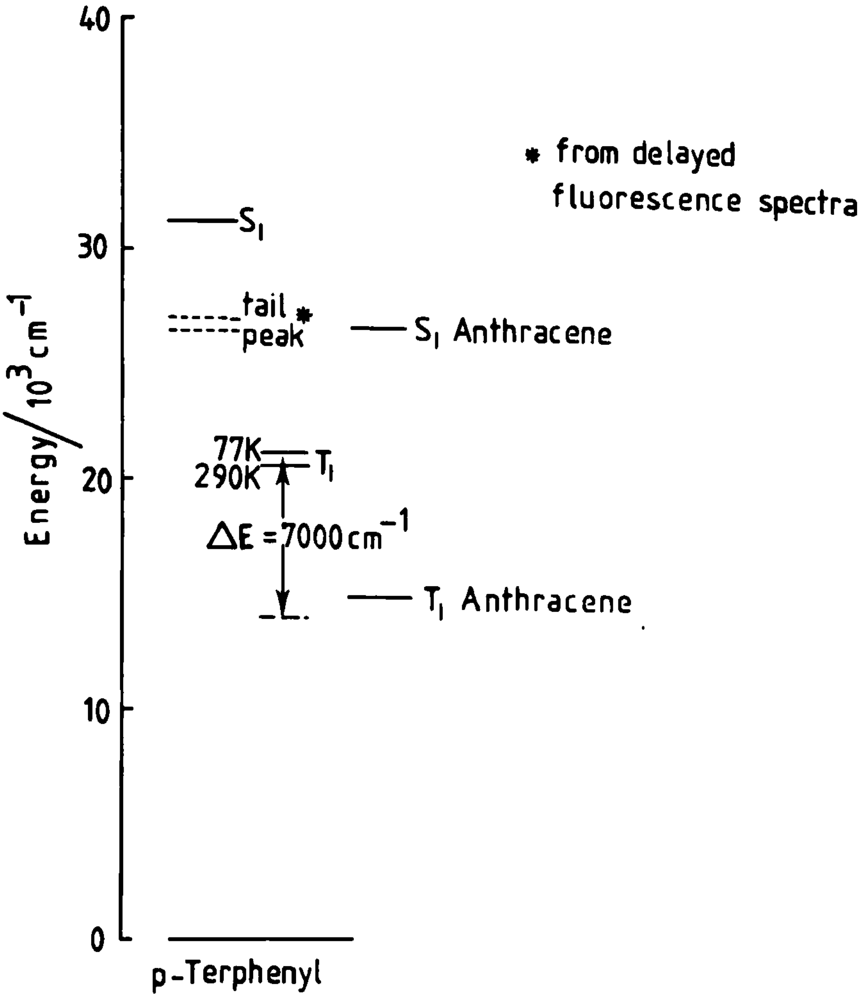


FIGURE 7 Energy level diagram.

pleted at similar rates, the former by deactivation and trapping and the latter by deactivation and thermal release.

The effect of changing the chopping frequency may be seen in Figure 5 (d and e). The fast rise is apparent in both profiles and reflects the fact that the chopping rate ω is not sufficiently small with respect to r and s at 190 K. Halving the chopping rate (see Figure 5e) decreases the ratio, ρ, between the fast and slow components in the decay, reflecting the fact that with lower ω the trap may be more completely deactivated before the onset of the "on" cycle.

Nature of the trap

It is apparent that a deep triplet trap controls the steady state and time dependent delayed fluorescence behavior of our *p*-terphenyl single crystals. The centers responsible for this trap also serve to trap the singlet exciton following first excitation into the triplet state. The trap is not, however, observable in prompt fluorescence measurements affecting neither the spectrum nor the singlet lifetime to any marked extent. An energy level diagram relevant to our crystals is schematically shown in Figure 7 and all the experimental data are consistent with an assignment of the trap to anthracene molecules at a concentration of 10^{12}–10^{13} molecules cm^{-3} i.e. 10^{-8}–10^{-9} mole/mole. The occurrence of the phase transition at *ca* 190 K does not greatly perturb this trapping behavior but there does appear to be a faster rate of decrease of the intensity of delayed fluorescence and the triplet decay rate at *ca* 220 K. A hysteresis between heating and cooling cycles in I_{DF}/T dependences also occurs at 190 K. It is likely that if the phase transition introduces triplet traps into the *p*-terphenyl lattice as a result of the slight displacement/misorientation of molecules then these are too shallow to be observable in the present experiments. To study this and other related phenomenon in detail requires further crystal purification to reduce the anthracene content below 10^{-10} mole/mole.

Acknowledgments

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