Exciton Fission and Annihilation in Crystalline Tetracene

Graham R. Fleming, David P. Millar, Graeme C. Morris, John M. Morris and G. Wilse Robinson

A Department of Physical Chemistry, University of Melbourne, Parkville, Vic. 3052.
B Present address: The Royal Institution, 21 Albemarle Street, London, W1X 4BS, U.K.
C Department of Physical Chemistry, University of Queensland, St Lucia, Qld. 4067.
D Present address: Department of Chemistry, Texas Tech University, Lubbock, Texas 79409, U.S.A.

Abstract
The time-resolved fluorescence of tetracene crystals excited by a single 7-ps pulse of 530-nm light has been measured with a streak camera/OMA system. The singlet exciton lifetime was found to be \(300 \pm 30 \text{ ps}\) at 293 K. Singlet-singlet exciton annihilation was observed, and the rate constant found to be \(5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}\). In order to fit the observed decay curves, an upper limit of \(c. 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}\) must be set on the singlet-triplet exciton annihilation rate. The measured singlet-singlet exciton annihilation rate is consistent with a hopping model for singlet exciton motion at room temperature.

Introduction
The fission of a singlet exciton into two triplet excitons in crystalline tetracene has been the object of considerable attention since it was first suggested by Swenberg and Stacy. This spin-allowed process competes so efficiently with normal fluorescence at room temperature that the fluorescence quantum yield of tetracene crystals is only 0.002, and the fluorescence lifetime is less than a nanosecond, compared with 5.5 ns in the gas phase. Previous measurements of the crystal fluorescence lifetime have varied from 100 to 300 ps, but these measurements have all been limited by instrumental factors. Recently, Heisel et al. have measured the fluorescence decay kinetics of tetracene crystals and shown that exciton annihilation was important when the high power densities from mode-locked lasers were used for excitation. However, their measurements were also considerably hampered by a slow instrumental response (\(\geq 100 \text{ ps}\) risetime). In this paper, we present fluorescence decay curves, obtained with our streak camera/OMA system, essentially free of slow

instrumental response problems. By analysing a series of fluorescence decay curves, we have been able to obtain rate constants for the singlet exciton decay and for singlet exciton annihilation.

Experimental
Single crystals of tetracene were grown from the vapour, under 150 Torr of pure nitrogen, from 99.95% pure tetracene (Princeton Organics). Sublimation flakes (c. 3 by 5 mm in area) were suspended from thin glass fibres and excited by a single 7-ps pulse of 530-nm light (obtained by frequency doubling a pulse selected from the pulse train of a mode-locked Nd:glass laser; see Figs 6 and 7 of ref.9). The maximum excitation density was $5 \times 10^{15}$ photons cm$^{-2}$; lower excitation densities were obtained by inserting neutral density filters in the laser beam. With the sweep speed used for collecting most of the data, the resolution of the system was limited by the streak camera slit width to c. 10 ps (the FWHM of the approximately Gaussian-shaped response function). A range of curves were obtained, dependent on the excitation density. Only curves in which the intensity decreased to $1/e$ of the initial intensity at times greater than c. 100 ps were used for the analysis, so any distortion of the decay curves by the exciting pulse in this time region was negligible. Thus it was unnecessary to deconvolute the exciting pulse from these decay curves.

Results
Fig. 1 shows fluorescence response curves obtained at the highest excitation density (b) and the lowest excitation density which provided sufficient fluorescence for accurate streak camera detection (a). As the excitation density increased, the time

\[ \text{Fig. 1. Fluorescence response of a single tetracene crystal excited by a 530-nm pulse. The excitation densities were (a) } 3 \times 10^{14} \text{ photons cm}^{-2}, \text{ (b) } 5 \times 10^{15} \text{ photons cm}^{-2}. \]  
The smooth curve in (a) was calculated from equation (3) or (8).

for the fluorescence intensity to decrease to $1/e$ shortened from 150 to 30 ps. None of the curves could be fitted to a single exponential over the entire decay. These curves clearly indicate that processes other than first-order decay are occurring; we have considered all the likely processes in the following kinetic equations:

\[ \frac{dN_S}{dt} = -\alpha_s N_S - \gamma_{SS} N_S^2 - \gamma_{ST} N_S N_T + \frac{1}{2} f \gamma_{TT} N_T^2 \]  
\[ \frac{dN_T}{dt} = -\alpha_T N_T + 2k_{nr} N_S - \frac{1}{2}(1 + f) \gamma_{TT} N_T^2 \]  
\[ \alpha_s, \alpha_T \text{ are the first-order decay rate constants for the singlet and triplet excitons} \]

\[ \alpha_s = k_r + k_{nr} + k_f \]  

where $k_r$, $k_{nr}$ and $k_f$ are the radiative, non-radiative and fission rates respectively, $k_{nr}$ will include the rate of host-to-trap energy transfer if singlet exciton traps are present. The terms $\gamma_{SS}$, $\gamma_{ST}$ and $\gamma_{TT}$ are the rate constants for singlet–singlet, singlet–triplet and triplet–triplet exciton annihilation respectively; $f$ is the fraction of triplet–
triplet annihilations producing a singlet exciton. The coupled differential equations (1) and (2) were solved numerically by a modified Runge–Kutta procedure, and by using such values for the parameters as could be found in the literature or estimated from data for other crystals. A natural initial assumption is that singlet–singlet annihilation is the only important process in addition to fission and normal radiative and non-radiative decay. However, Ern et al. have estimated $\gamma_{TT}$ to be $2 \times 10^{-9}$ cm$^3$ s$^{-1}$ and $\gamma_{ST}$ $2 \times 10^{-7}$ cm$^3$ s$^{-1}$, and recently Heisel et al. estimated $\gamma_{ST}$ as $5 \times 10^{-9}$ cm$^3$ s$^{-1}$. Thus it is essential, since a high concentration of triplet excitons is produced by the fission process, to determine whether singlet–triplet and triplet–triplet annihilation are important. The parameters used were

$$N_s(0) = 10^{18} \text{ cm}^{-3},$$ a typical initial singlet exciton concentration under our excitation conditions;

$$N_T(0) = 0;$$

$$\alpha_T = 0,$$ since the rate of triplet decay is negligible compared with other rates ($\alpha_T = 1.6 \times 10^4$ s$^{-1}$, ref.11); and

$$\alpha_S = 3 \times 10^9 \text{ s}^{-1}$$ (ref.6).

The remaining parameters, $\gamma_{SS}$, $\gamma_{ST}$, $\gamma_{TT}$ and $f$, were varied to determine what ranges of their values would produce fluorescence decay curves of the same form as those observed. The results of these trials may be summarized as follows:

(i) The value of $\gamma_{TT}$ has little effect on the fluorescence decay in the short time regime considered here (up to 500 ps after the exciting pulse). Values in the range $0-10^{-9}$ cm$^3$ s$^{-1}$ gave practically identical curves; consequently, the value of $f$ also has negligible effect in the first 500 ps.

(ii) If the value of $\gamma_{ST}$ is made similar to or larger than $\gamma_{SS}$, then the calculated curve shows an initially slow decay rate, which increases as the triplet population builds up. For example, with $\gamma_{ST} = 6 \times 10^{-9}$ cm$^3$ s$^{-1}$, $\gamma_{SS} = 6 \times 10^{-9}$ cm$^3$ s$^{-1}$, the rate of fluorescence decay reaches a maximum at c. 150 ps, and then decreases again at later times. Some typical results are shown in Fig. 2. In the observed decay curves, the rate of fluorescence decay is always greatest at time zero and decreases from then on. This form of decay curve can only be simulated with the kinetic scheme

$\gamma$ values (cm$^3$ s$^{-1}$)

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<tr>
<th>$\gamma_{SS}$</th>
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Fig. 2. Singlet exciton densities as a function of time, calculated from equations (1) and (2). $\gamma$ parameters are indicated on the graph.

$\alpha_S = 3 \times 10^9 \text{ s}^{-1},$

$k_f = 2 \times 10^9 \text{ s}^{-1}$ and

$f = 1$ for all curves.

A rescaled experimental curve is also shown.

represented by equations (1) and (2) if $\gamma_{SS} > \gamma_{ST}$. Therefore, our results demonstrate that singlet–triplet annihilation is unimportant relative to singlet–singlet annihilation and enable us to set an upper limit on the singlet–triplet annihilation rate, $\gamma_{ST} \leq 0.2 \gamma_{SS}$. Values of $\gamma_{ST}$ in the range $0.0 < 0.2 \gamma_{SS}$ produce identical curves in the short time regime. This result differs from that of Heisel et al.\textsuperscript{8} who put $\gamma_{SS} \approx \gamma_{ST}$. The discrepancy may be attributed to their instrumental response function, which contained significant components at times up to 1 ns. Setting $\gamma_{ST} = \gamma_{TT} = 0$ in equation (1) enables the following analytic solution for the fluorescence intensity $I(t)$, which is valid for the short time regime, to be found:

$$I(t) = \alpha_s I(0)/(\{\alpha_s + \gamma_{SS} N_0 \exp(\alpha_s t) - \gamma_{SS} N_0\}$$

(3)

Using an initial estimate for $\alpha_s$, we may transform equation (3) into a linear equation

$$y = a + bx$$

(4)

by the substitution

$$y = 1/I(t) \quad x = \exp(\alpha_s t)$$

(5)

In equation (4)

$$a = -\gamma_{SS} N_0/\alpha_s I_0 \quad b = (\alpha_s + \gamma_{SS} N_0)/\alpha_s I_0$$

(6)

By means of a weighted linear regression, the best values for $a$ and $b$ were found, from which an initial estimate for $\gamma_{SS} N_0$ was calculated; $\alpha_s$ was then varied and a new value for $\gamma_{SS} N_0$ determined. This process was continued until the best values of both $\alpha_s$ and $\gamma_{SS} N_0$ for ten separate decay curves, excited at the same intensity, were found (using a least-square residuals criterion). The best values were:

$$\alpha_s = (3.3 \pm 0.3) \times 10^9 \text{s}^{-1}$$

$$\gamma_{SS} N_0 = (5 \pm 1) \times 10^9 \text{s}^{-1}$$

The initial average exciton density $N_0$ was calculated from

$$N_0 = N_p[1 - \exp(-\kappa l)/l]$$

(7)

where $N_p$ is the photon density of the exciting pulse, $\kappa$ is the crystal absorption coefficient at 530 nm, $l$ is the penetration depth, defined as the point at which the incident light is reduced to $1/e$ of its initial intensity. Equation (7) makes the assumption, which is readily verified, that excitons neither diffuse out of the excited volume, nor are quenched at the surface.\textsuperscript{*} Using $\kappa = 5 \times 10^3 \text{cm}^{-1}$, an estimate from the absorption spectra,\textsuperscript{13} and $N_p \approx 3 \times 10^{14}$ photons $\text{cm}^{-2}$, we obtain $N_0 = 10^{18} \text{cm}^{-3}$. Thus $\gamma_{SS} = 5 \times 10^{-9} \text{cm}^3 \text{s}^{-1}$. The uncertainty in $N_p$ due to shot-to-shot variations in the exciting pulse intensity is quite high, probably about 50\%.

\textsuperscript{*} The singlet exciton diffusion length is estimated to be $d = 120 \text{Å},$\textsuperscript{12} which is negligible compared to the dimensions of the excited volume. The fraction of excitons which may diffuse to the surface is:

$$\int_0^z N_p \exp(-\kappa x) \, dx / \int_0^\infty N_p \exp(-\kappa x) \, dx = 1 - \exp(-\kappa d) \approx 0.01$$


When the depth dependence of the exciton density is included in the analysis, equation (3) should be replaced by

\[ I(t) = I(0)[(\kappa + \kappa_1)/\kappa N_p] \int_0^\infty N_s(x,t) \exp(-\kappa_1 x) \, dx \]  

(8)

The attenuation of fluorescence from within the crystal due to reabsorption is included in (8) under the assumption that the reabsorption may be represented by a single effective absorption coefficient \( \kappa_1 \).

This approximation is often made in reabsorption studies of the anthracene crystal.\(^{14}\) No attempt has been made to include the additional complication of re-emission of fluorescence following reabsorption. The range of integration was extended to infinity because the crystal thickness is very large compared to the penetration depth. The integral was then suitable for evaluation by Gaussian quadrature. The singlet exciton density in (8) is given by

\[ N_s(x,t) = \frac{\alpha_s N_s(x,0)}{[\gamma_{ss} N_s(x,0)] \exp(\gamma_{ss} t) - \gamma_{ss} N_s(x,0)} \]  

(9)

where the initial singlet exciton density is determined by Beer's law

\[ N_s(x,0) = \kappa N_p \exp(-\kappa x) \]

From the previous values for the parameters \( N_p \) and \( \kappa \), and various values of \( \kappa_1 \), the best fit of equation (8) to the ten decay curves was found by varying \( \alpha_s \) and \( \gamma_{ss} \). For \( \kappa_1 \) in the range \( 0 \leq \kappa_1 \leq 5 \times 10^3 \) cm\(^{-1}\), the fitted curves were essentially identical to those obtained from equation (3). The room temperature emission spectrum of tetracene single crystals consists of two broad structureless bands at 560 (maximum) and 610 nm. The crystal absorption in this region is very weak,\(^{13}\) so that the absorption coefficient at 530 nm, \( 5 \times 10^3 \) cm\(^{-1}\), is an upper limit for \( \kappa_1 \). The first-order decay rate was \( \alpha_s = 3.3 \times 10^9 \) s\(^{-1}\) for all \( \kappa_1 \), and is identical to the result from equation (3). This is expected, since the crystal lifetime will only vary because of fluorescence re-emission. However, the annihilation rate \( \gamma_{ss} \) varies from \( 7 \times 10^{-9} \) cm\(^3\) s\(^{-1}\) when \( \kappa_1 = 0 \) to \( 5 \times 10^{-9} \) cm\(^3\) s\(^{-1}\) when \( \kappa_1 = 5 \times 10^3 \) cm\(^{-1}\).

Discussion

The value of the singlet exciton first-order decay rate found here, \( \alpha_s = 3.3 \times 10^9 \) s\(^{-1}\) at 293 K, corresponding to a singlet exciton lifetime \( \tau_s = 300 \) ps, agrees well with some previous measurements, notably those of Smith and Weiss,\(^6\) who found the same value using much lower excitation densities (c. \( 10^{17} \) photons cm\(^{-2}\) s\(^{-1}\)). At least two much shorter singlet exciton lifetimes have been measured,\(^4,5\) but these may be directly attributed to (a) the high excitation densities used without allowance for the exciton annihilation and (b) the use of the light gate technique, with its inherent inaccuracies masking the non-exponential nature of the decay curves. It is well known that host crystal lifetimes decrease with added impurities or defects, due to the deactivation of singlet excitons by host-to-trap energy transfer.\(^{15}\) The fluorescence lifetime thus provides some guide to crystal purity. While the explicit


details of how the lifetime of tetracene excitons is affected by impurities are unknown, we note that the 300-ps lifetime measured here is the longest reported to date.

Lopez-Delgado et al. used weak synchrotron radiation to excite tetracene crystal fluorescence and fitted a dual exponential to the decay curves, with 0.2 and 1.7 ns lifetimes. The discrepancy between their 0.2 ns decay and the 0.3 ns lifetime measured by us may be ascribed to the problem of fitting a dual exponential function to a decay curve convoluted with a 0.6 ns FWHM instrumental response function.

The singlet exciton fission rate at 293 K can be estimated by assuming the sum \( k_r + k_{nr} \) is temperature-independent and using the value for \( k_r + k_{nr} \) found by Smith and Weiss in the 100–230 K range:

\[
k_r = \gamma_s - (k_r + k_{nr}) = 2 \times 10^9 \text{ s}^{-1}
\]

In the decay curves from the single crystals, we did not observe the long-lived component seen by Lopez-Delgado et al. In our curves, taken with slow streak camera speeds, a long decay component with an intensity greater than about 5% of the major fast component would have been readily discernible. Therefore we conclude that any long-decaying component accounts for at most about 1% of the pure crystal fluorescence. However, we did observe a second component with a lifetime in the 1–2 ns region when polycrystalline films grown in air were excited. The polycrystalline samples may contain singlet traps which provide the long-decaying emission, an explanation advanced by Heisel et al. to explain the slower decay observed by Lopez-Delgado et al.

Calculations using equations (1) and (2) show that there is a long-lived fluorescence, apparent after about 500 ps, which is due to singlets created by triplet–triplet annihilation. For \( \gamma_{TT} = 2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \), the value used by Heisel et al., the contribution of the long-lived fluorescence is greater than 5% of the total fluorescence. Since the fluorescence we have observed in the long time region is very weak, this value for \( \gamma_{TT} \) is probably too large for pure crystals. A recent study by Arden et al. found \( \gamma_{TT} = 10^{-11} \text{ cm}^3 \text{ s}^{-1} \), a value which is consistent with our observations.

The value of the singlet–singlet exciton annihilation rate, \( \gamma_{ss} \), found from equation (3), agrees with that found by Heisel et al. Both results apply to a uniform exciton density, and so the agreement allows us to place some confidence in the value \( \gamma_{ss} = 5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \). However, the neglect of the depth dependence of the exciton density may lead to apparently smaller values of \( \gamma_{ss} \). The correction to \( \gamma_{ss} \) may be as much as 40%, depending on the magnitude of reabsorption, but is within the limits of experimental uncertainty.

If the singlet exciton motion is considered as a random walk from one molecule to its nearest neighbour lattice site, and singlet–singlet annihilation is presumed to occur by the interaction of two singlet excitons on neighbouring lattice sites, then a diffusion rate for exciton migration may be defined:

\[
D = \frac{\gamma_{ss}}{8\pi R}
\]

where \( R \) is the average lattice spacing. Substituting \( \gamma_{ss} = 5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \) in equation (8) gives \( D = 2 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \). The average distance the singlet exciton migrates

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during its lifetime, \( d \), is related to \( D \) by\(^{15}\)

\[
d = (2D\tau_s)^{1/2}
\]  

(11)

where \( \tau_s = 1/\chi_s = 300 \) ps, giving \( d = 110 \) Å. Vaubel and Baessler have measured both these quantities,\(^ {12}\) obtaining \( D = 1.7 \times 10^{-3} \) cm\(^2\) s\(^{-1}\) and \( d = 120 \) Å. Thus our value of \( \gamma_{ss} \) is consistent with a hopping model of singlet exciton motion at room temperature. Several different studies have produced a similar conclusion for singlet exciton motion in anthracene at 300 K.\(^ {18}\)

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