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Energy Transfer in Perylene Doped Anthracene Crystals

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Time resolved spectroscopy with ultraviolet light excitation was used to investigate host sensitized energy transfer in perylene doped anthracene crystals. The UV excitation leads to a wavelength dependence of the host fluorescene decay time due to the effects of reabsorption. The time resolved spectroscopy results are shown to be consistent with the generalized random walk model for energy transfer with the same exciton hopping time found previously for tetracene doped anthracene but a smaller capacity. It is speculated that the latter is due to a smaller, more symmetric extended trapping region around each impurity molecule.

INTRODUCTION

A generalized random walk model for exciton migration was recently proposed to explain the observed time dependence of the energy transfer rate in doped organic crystals.[1] To check the validity of this theory, it is necessary to apply it to results obtained on a variety of host-activator systems, and this paper deals with the specific system of perylene doped anthracene. Also, previous investigations were performed using bulk excitation provided by an X-ray or laser (two-photon absorption) source,[2] whereas the present work utilized surface excitation provided by an ultraviolet source. The results are compared to previous investigations of tetracene doped anthracene and are shown to be consistent with the generalized random walk model.

EXPERIMENTAL

The samples were vapor grown crystals with approximate dimensions of 1 × 0.5 × 0.1 cm and perylene concentrations on the order of 10^{18} cm^{-3}. The time dependence of the fluorescence was monitored using the equipment shown in the block diagram in Figure 1. The samples were excited by a hydrogen filled spark gap oscillator with a repetition rate of approximately 35 kHz and a pulse half-width of about 1.5 nsec. The exciting light was passed through color filters to selectively excite either the anthracene or perylene and the fluorescence wavelength to be monitores was selected by a 0.3 m Spex monochromator before being detected by an RCA 8850 (S-4) photomultiplier tube. Signals from the light pulser and the phototube were sent to the start and stop inputs of a time to pulse hieght converter, respectively. The signal taken from the ninth stage dynode of the phototube was passed through a single channel analyzer set to pas only single photon events. This signal was used to gate the output of the time to pulse height converter so that only single photon events were sent to the multichannel analyzer. The resulting signal was displayed on an oscilloscope and recorded on a strip chart recorder. Most of this electronic equipment is made by Ortec.

When undoped anthracene crystals are excited by UV radiation, excitons are created near to the surface of the sample due to the high absorption coefficient. Because of the overlap of the emission and absorption spectra, much of the fluorescence emitted in the high energy region of the spectrum is reabsorbed and subsequently can be re-emitted at lower energies where reabsorption does not

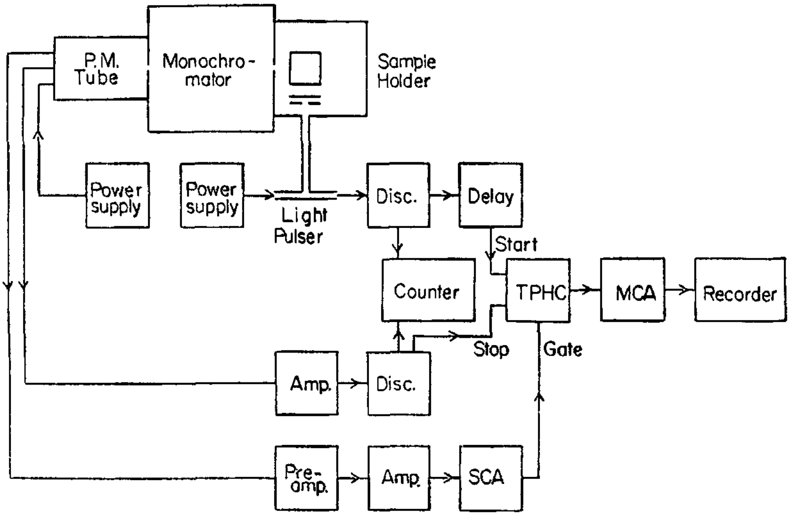


FIGURE 1 Block diagram of the time resolved spectroscopy apparatus.

occur. This distorts the observed fluorescence spectrum by enhancing the low energy bands with respect to the high energy bands. It also leads to a wavelength dependence of the flurorescence lifetime as shown in Figure 2. The majority of fluorescent photons detected at short wavelengths have escaped without being reabsorbed and a short decay time is measured at these wavelengths. At long wavelengths, most of the fluorescent photons are detected after they have beeen reabsorbed at shorter wavelengths and a much longer decay time is measured in this region. Measurements were made on freshly cleaved samples to eliminate the quenching of excitons at surface oxide layers.

INTERPRETATION

These reabsorption effects make it difficult to interpret time resolved spectroscopy data in doped crystals. The majority of the total fluorescence appears at long wavelengths and has the long lifetime characteristic of reabsorption. However, at these wavelengths, the anthracene fluorescence and perylene fluorescence overlap and cannot be monitored separately. The time dependence of the anthracene fluorescence monitored at short wavelengths cannot be taken as an indication of the time dependence of the exciton concentration in the crystal

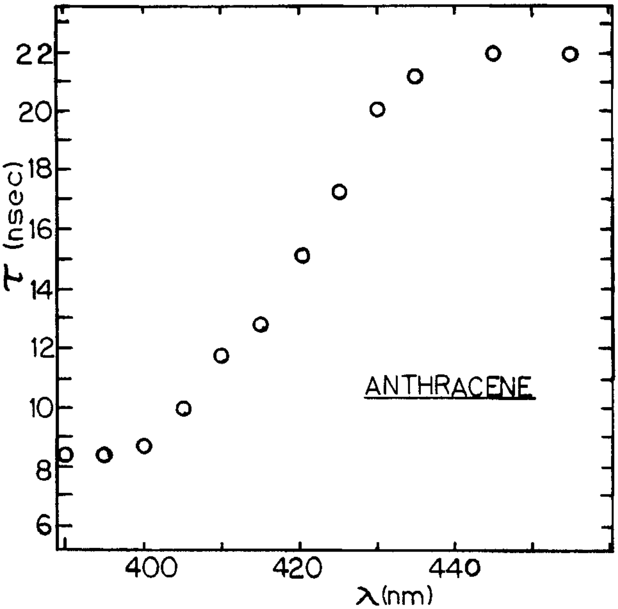


FIGURE 2 Wavelength dependence of the fluorescence decay time of an anthracene crystal under ultraviolet light excitation.

since only a small portion of the exciton fluorescence is emitted in this short lifetime region. Also, the short wavelength fluorescence is not quenched with perylene concentration as much as the long wavelength fluorescence since the short lived excitons do not transfer energy as efficiently as the long lived excitons.

Only the time dependence of the perylene fluorescence is meaningful in characterizing energy transfer because of the above considerations. Figure 3 shows the time evolution of the perylene fluorescence of a sample with 4.6×10^{18} cm^{-3} perylene molecules. The circles represent the experimental data, and the solid line is the best theoretical fit to the data. The same best fit is predicted by two theories, the combined theory of exciton diffusion and long range resonant interaction of Yokoto and Tanimoto[3,4] and the generalized random walk model.[1] In previous investigations, the adjustible parameters involved in these theories were uniquely obtained by requiring a simultaneous fit to both the sensitizer and activator fluorescence data.[1,2] Unfortunately, with only the perylene curve to fit, it isn't possible to obtain unique values for the parameters in this case. However, we do find that it is impossible to fit the data with the combined theory using physically reasonable parameters for both the diffusion coefficient and the trapping radius. The fit shown in Figure 3 was obtained for a large trapping radius and small diffusion coefficient, which is similar to what was found for tetracene doped anthracene.

In the generalized random walk model for delta function excitation, the expression describing the activator fluorescence is[1]

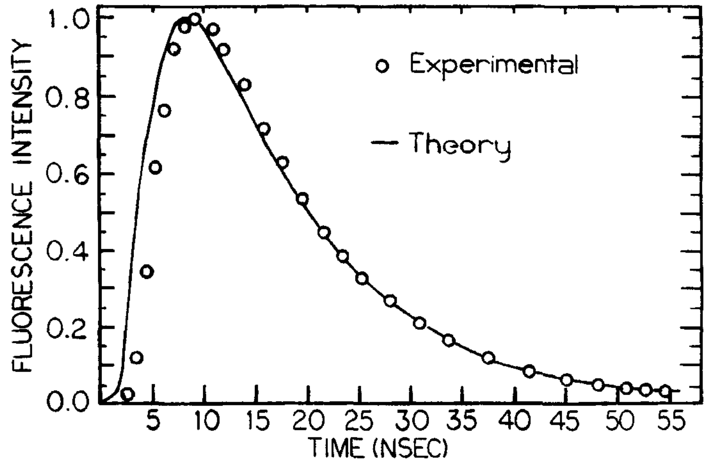


FIGURE 3 Time dependence of the fluorescence of perylene in anthracene. The perylene concentration is 4.6×10^{18} cm^{-3}. The circles represent experimental data and the line the best theoretical fit as discussed in the text.

$$I_a(t) \propto n_a(t) = e^{-\beta_a t} \int_0^t e^{\beta_a t'} n_s(t') \left\{ N_a C(A) t_H^{-1} + \left(\frac{2N_a C(A)^2 t_H^{-\frac{1}{2}}}{(2\pi\sigma^2)^{3/2}} \right) t'^{-\frac{1}{2}} \right\} \mathrm{d}t' \quad (1)$$

where

$$I_s(t) \propto n_s(t) = \exp\left[-(\beta_s + N_a C(A) t_H^{-1}) t - \left(\frac{4N_a C(A)^2 t_H^{-\frac{1}{2}}}{(2\pi\sigma^2)^{3/2}} \right) t^{\frac{1}{2}} \right]. \quad (2)$$

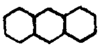
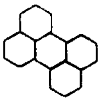
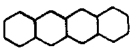
Here, $n_s(t)$ and $n_a(t)$ are the concentrations of sensitizer and activator excited states, respectively; N_a is the concentration of activator molecules, with fluorenscence decay rates of β_s and β_a, and $C(A)$ is the capacity of the random walk, which in the limit of many hops gives the number of new sites sampled by the exciton on each hop, and t_H is the hopping time. σ is a parameter which depends on the hopping probabilities for hops of different lengths and in different directions on a specified lattice. $2\sigma^2$ has been calculated for various step length distributions for a simple cubic lattice with one molecule per unit cell and for an anisotropic random walk $2\sigma^2 \approx \frac{1}{2}$. We use this value and the measured fluorescence decay times of anthracene (22.1 nsec) and perylene (12.5 nsec) and treat t_H and $C(A)$ as adjustible parameters to fit the data. The finite width of the excitation pulse is accounted for by treating it as a series of equally spaced delta functions. The best fit resulting from this procedure is shown in Figure 3 and is obtained using $C(A) = 12$ and $t_H = 3 \times 10^{-11}$ sec.

DISCUSSION AND CONCLUSIONS

Table I lists the parameters needed to fit the perylene doped anthracene data and compares them to those obtained on tetracene doped anthracene.[1] As dis-

TABLE I

Summary of time resolved spectroscopy data

Host	Activator	$R_0(A)$	$C(A)$	t_H (sec)
Antracene 	Perylene 	26	12	3×10^{-11}
	Tetracene 	30	35	3×10^{-11}

cussed above, the parameters for fitting the perylene doped anthracene data are not unique. However, since the hopping time of the exciton does not depend on the type of activator, we use the value of $t_H = 3 \times 10^{-11}$ sec found for tetracene doped anthracene and this gives $C(A) = 12$. Since the assumed value of $2\sigma^2 = 0.5$ applies to an anisotropic random walk on a simple cubic lattice with one molecule per unit cell whereas anthracene is monoclinic with two molecules per unit cell, the numerical values listed for the parameters in the table must be considered only as rough estimates. However, they do indicate the relative differences between systems.

The capacity of the random walk is effected by the size and shape of the trapping region and by the importance of greater than nearest neighbor steps. Since the stepping probabilities are not dependent on the type of activator in a given host, the different values of $C(A)$ listed in Table I must be characteristic of the trapping region. The size and shape of the trapping region depends on both the distortion of the host lattice sites due to the presence of an impurity molecule and on the strength of the dipole-dipole interaction between host and activator molecules. The latter is characterized by the critical interaction distance R_0 given by

$$R_0 = \left(\frac{5.86 \times 10^{-25} \phi_s}{n^4 \bar{\nu}_{sa}^4} \int g_s(\bar{\nu}) G_a(\bar{\nu}) \mathrm{d}\bar{\nu} \right)^{1/6} \tag{3}$$

where ϕ_s is the quantum efficiency of the sensitizer, n is the refractive index of the crystal, $g_s(\bar{\nu})$ and $G_a(\bar{\nu})$ are the spectral distribution functions of the sensitizer emission and activator absorption spectra, respectively, and $\bar{\nu}_{sa}$ is the mean wave number in the region of spectral overlap. Figure 4 shows the spectral overlap of perylene in anthracene[5] which leads to a value of $R_0 = 26$ A. Since this is only slightly smaller than the value for tetracene doped anthracene, it appears that the much smaller capacity is due to smaller host distortion. Table I of Ref. 1 shows some values for the capacity culculated for different sizes and shapes of trapping regions. The comparison of molecular shapes shown in our Table I implies a linear trapping region for tetracene in anthracene and a more symmetric trapping region for perylene. The calculations of Ref. 1 shows the former shape should give rise to a larger value for the capacity, which is consistent with what we find. The value of 12 is probably consistent with a trapping region which includes all host molecules within three or four nearest neighbor sites, but, as emphasized previously, the exact numerical results cannot be taken too seriously.

Table II lists the energy transfer rate constants reported for perylene in other hosts obtained by other experimental means. The value found by Northrop and Simpson[6] for perylene doped anthracene is close to the value we obtained. The small difference could be due either to inaccuracies in measuring the impurity

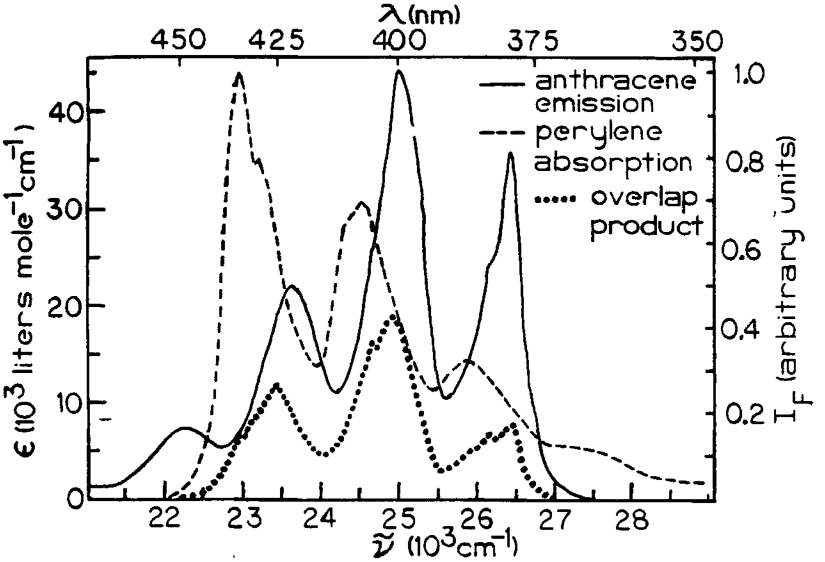


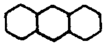
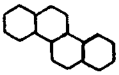
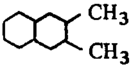
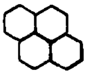
FIGURE 4 Emission spectrum of anthracene, absorption spectrum of perylene, and their spectral overlap product. The spectra shown were obtained on our samples, but the numerical values for the molar extinction coefficient were taken from Ref. 5 and the relative peak heights for the anthracene fluorescene were adjusted in comparison to Ref. 5 to eliminate reabsorption effects.

concentration or to different exciton lifetime for different experimental conditions. The energy transfer rate appears to be slightly smaller for perylene in a chrysene host[7] and slightly larger for perylene in 2,3-dymethylnaphthalene.[8] These hosts have different crystal structures than anthracene and the small self-overlap of their absorption and emission spectra indicates exciton hopping times will probably be longer. The overlap of the emission spectra of these hosts with the perylene absorption is less than in anthracene, implying a smaller critical interaction distance. Size considerations seem to indicate that host distortions due to perylene impurities will be greater in 2,3-dimethylnaphthalene and smaller in chrysene as compared to anthracene. This would lead to proportional changes in $C(A)$ and, thus, changes in the energy transfer rate. The energy transfer rate in pyrene crystals is reported to be about the same as in anthracene,[5] but the situation is complicated by the formation of excimers.[9]

In summary, results for the time dependence of the energy transfer rate are obtained for perylene doped anthracene crystals excited by UV light are similar to those obtained previously on other systems excited by bulk excitation. These results are consistent with the generalized random walk model for exciton migration and trapping.

TABLE II

Exiton trapping constants for perylene

Activator	Host	k	Method	Reference
Perylene 	Anthracene 	8.8×10^3	$C(A)t_H^{-1}\,\tau_s^0$	this paper[a]
		1.9×10^4	$\frac{I_s^0 - I_s}{I_s N_a}$	(6)
	Chrysene 	1.1×10^3	$(\tau_s^0/\tau_s - 1)/N_a$	(7)
	2,3-Dimethyl-naphthalene 	8.7×10^4	$(\tau_s^0/\tau_s - 1)/N_a$	(8)
	Pyrene 	1.2×10^4	$\frac{I_s^0 - I_s}{I_s N_a}$	(6)

[a] This is the constant asymptotic value $k(\infty)\,\tau_s^0/N_a$.

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