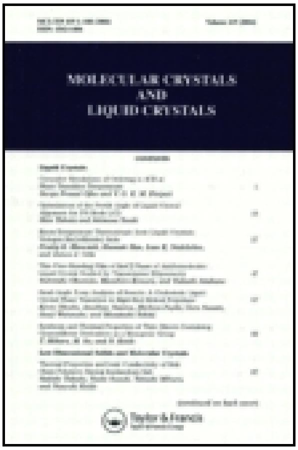

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Exciplex Emission from Perylene- Doped 9- Cyanoanthracene Crystals

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Exciplex Emission from Perylene-Doped 9-Cyanoanthracene Crystals

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Perylene-doped 9-cyanoanthracene crystals show exciplex emission at 520 nm with a decay time of about 120 nsec. Transfer of energy from excimer to exciplex is efficient at high temperatures despite the small trap depth. At 77°K the exciplex lies 1100 cm^{-1} above the excimer and yet no transfer from exciplex to crystal occurs. The estimated excimer-exciton parameters are: $t_H \approx 10^{-11}\ \text{sec}^{-1}$, $D_z = 8 \times 10^{-5}\ \text{cm}^2/\text{sec}$, $L_z = 330$ Å.

INTRODUCTION

The first unequivocal exciplex emission in solution was reported by Leonhardt and Weller[1] in 1963. The exciplex[2,3] as well as the excimer[4–6] phenomena have been the subjects of extensive investigations, since it is believed that these species are intermediates in various photochemical reactions, and since there have been recent applications of such systems for production of powerful lasers.[7] The one crystalline system which has been interpreted as showing exciplex emission[8] is that of pyrene doped with perylene. However, since the initial publication this interpretation has been the subject of controversy amongst various investigators.[8–12] Thus Kearns *et al.*[9,12] have argued that the anomalous emission originating from the perylene-pyrene system is due to reabsorption phenomena.

We report here on a different crystalline system which we believe to show exciplex emission unequivocally. We also point out the potential utilisation of crystalline systems of known packing arrangements to provide understanding of some of the geometrical factors related to exciplex formation.

EXPERIMENTAL

9-Cyanoanthracene (9-CNA) was purified by photodimerization in deareated solutions, followed by thermal splitting of pure photodimer under vacuum.

Samples of perylene-doped 9-cyanoanthracene for decay time measurements were prepared by cosublimation of perylene-9-CNA mixtures sealed off under vacuum and in some cases, subsequently melted and recrystallised from the melt.

Films were prepared by comelting and crystallising perylene 9-CNA mixtures between flat quartz or pyrex plates in a nitrogen atmosphere under red or yellow light.

Fluorescence measurements were performed on a modified Aminco Bowman spectrophotofluorometer as previously described.[13]

For lifetime measurements light from a TRW "nanosecond" deuterium lamp (model 31A) was passed through a Jarell–Ash ¼-meter grating monochromator or a Corning 7-54 filter and onto the sample. The emitted light was filtered and detected by a photomultiplier (Philips XP 1023), a multichannel analyzer system (Hewlett-Packard 5401-A), and an oscilloscope (Tektronix with 1S1 sampling unit). The lifetime was determined directly from the slope of a semilogarithmic plot of fluorescence against time.

RESULTS

I Emission spectra

a) *Room temperature* The emission spectra of 9-CNA crystals doped with perylene are structureless and the frequency at maximum intensity depends on dopant concentration. The red shift of the maximum of emission with increasing dopant concentration is summarised in Figure 1.

The shape of the emission band and the frequency of the band maximum were found to be independent of excitation wavelength.

b) *Liquid air temperature* For dopant concentrations below 10^{-2} M/M the shape of the emission band and the position of λ_{max} are indistinguishable from those of pure 9-CNA crystals and are independent of excitation wavelength. However, for and above 10^{-2} M/M dopant concentration the emission band is structureless but blue shifted compared to the emission of pure 9-CNA. The blue shift increases on increase in perylene concentration (not shown in figures). For 5×10^{-2} M/M of perylene concentration there is a difference between main (9-CNA) band excitation and tail band excitation: Main band-excitation ($\lambda <$ 400 nm) shows the blue shifted diffuse emission whereas tail band excitation (436 nm) results in a structural emission (see Figure 2). On raising the temperature slightly the longer wavelength peak disappears.

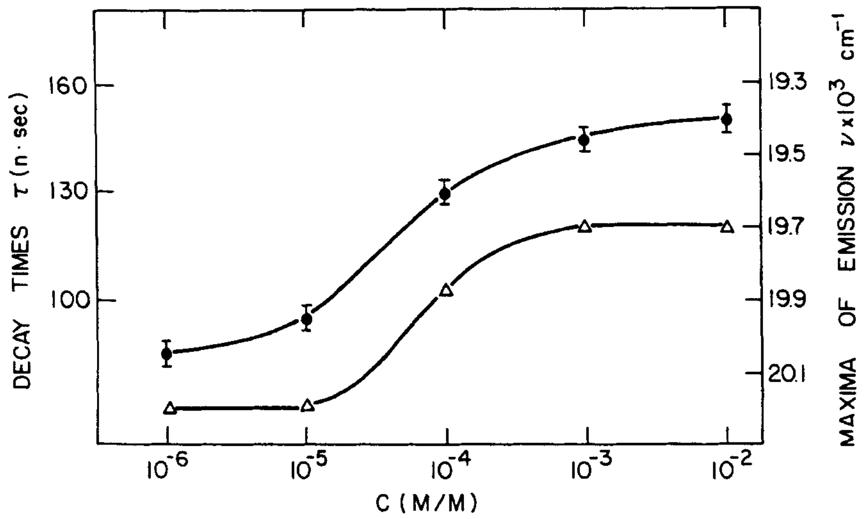


FIGURE 1 Decay times (ϕ) and fluorescence emission maxima (Δ) as a function of perylene (guest) concentration in 9-CNA crystal (host), at 300°K.

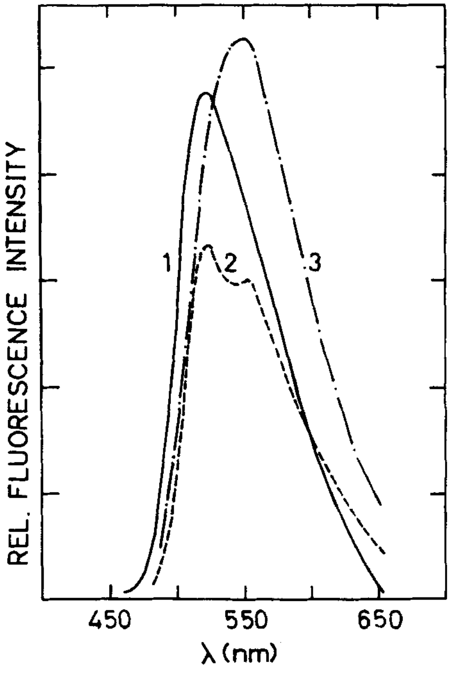


FIGURE 2 Corrected fluorescence spectra of 9-CNA polycrystalline films doped with perylene.

1 Excitation (300°K) at 365 nm, $C \approx 10^{-1}$ mole perylene/mole 9-CNA.

2,3 Excitation at 436 nm and 365 nm, respectively, $C \approx 5 \cdot 10^{-2}$ mole perylene/mole 9-CNA.

II Decay times

a) *Room temperature* Polycrystalline samples which were prepared by cosublimation show non-exponential decay. However, when such samples are then melted and recrystallised their decay curves can be fitted to a single exponent. In addition, the decay times of the emission from comelted samples are considerably longer than those of the slower-decaying part of the emissions from cosublimed ones (120 nsec compared to 80 nsec).

The results are summarised in Table I.

TABLE I

Decay times of emissions from 9-CNA host at different concentrations of perylene guest (293°K)

Sample	Dopant[a] concent. (M/M)	Sample preparation	Excitation λ (nm)	Wavelength detection[b] range	Decay time[c] (nsec)
1	10^{-6}	remelt	360	2B	70
			420	K-4	70
			450	K-4	70
2	10^{-5}	remelt	360	2B	70
			450	K-4	70
3	10^{-4}	remelt	360	K-4	100
			430	K-4	100
4	10^{-3}	remelt	360	K-4	120
			420	K-4	120
			450	K-4	120
5	10^{-2}	remelt	360	K-4	120
			420	K-4	120
			450	K-4	120
4	10^{-3}	cosublimed	360	2B	80[d]

[a] Input concentration only.
[b] 2B and K-4 Filters transmit light above 420 nm and 520 nm, respectively.
[c] Decay times obtained from semilogarithmic plots.
[d] This time is obtained from the slowest part of the fluorescence decay.

Polycrystalline films The results for polycrystalline perylene-doped films are summarized in Table II. The decays vary from film to film, with a considerable spread.

Effect of wavelength We investigated the excitation-wavelength effect on the decay times. Sample No. 5 in Table I was excited at 360 nm, in the main host absorption band, and at 450 nm, in the tail band of the host's absorption. The corresponding decay times are the same within the accuracy of the measurements. On the detection side it is possible to follow the decays of either all of the emission ($\lambda > 420$ nm) or of only that part above 520 nm.

TABLE II

Decay times of polycrystalline films of 9-CNA host and perylene guest (293°K)

Sample	Dopant concentration (M/M)	Excitation λ (nm)	Wavelength detection $\lambda >$ (nm)	Decay time[a] (nsec)
1	10^{-2}	330	520	120
2	10^{-2}	290	420	110
		420	520	110
		450	520	110
3	10^{-2}	230–415[b]	420	120
4	10^{-1}	230–415[b]	420	110
		230–415[b]	520	100
		420	520	110

[a] The decays showed a fast decay immediately after the flash, followed by a slow decay. Only the latter is shown in the Table.

[b] Corning glass filter No. 7-54.

The results in Tables I and II show that there is no significant difference between the decay time results obtained with these two filters.

b) *Liquid air temperature* At liquid air temperature the situation is different. We followed the decay times with filters transmitting only above 520 nm while exciting in the main absorption band of 9-CNA. The decay times (not listed in Tables) for perylene concentrations up to almost 10^{-2} M/M are similar to those of pure 9-CNA crystals.

DISCUSSION

Solubility of Perylene in 9-CNA It is obvious from the decay times presented in Table I (sample 4) that the cosublimation method of sample preparation is not suitable for the perylene-9-CNA pair and therefore only comelting methods were used. The possibility that undissolved microcrystals of perylene, in one or both known structures, are responsible for the shift in 9-CNA excimer emission was taken into consideration. The absorption spectrum of a film doped with 10^{-3} M/M perylene shows the lowest frequency absorption peak of perylene at 22,700 cm^{-1}. This value is close to that of the 0–0 transition of perylene in solution (22,800 cm^{-1}, benzene[14]) but differs from the values for perylene crystals[15] (20,800 cm^{-1}, crystalline β-form; 21,800 cm^{-1}, crystalline α-form). Also the emissions of our perylene-doped 9-CNA crystals show neither the structured monomeric β-perylene[16] emission ($\lambda_{max} \sim$ 560, 535 nm) nor the excimeric α-perylene[16] emission (λ_{max} 570 nm at 295°K). Even with 436 nm excitation, no perylene-doped emission could be detected. Finally, the decay times of perylene-doped 9-CNA crystals at room temperature are close to 120 nsec which should be compared to that of the perylene excimer emission (α-form crystals) which is about 40 nsec.[17,18]

Thus, we conclude that at least up to concentrations of 10^{-2} M/M most of the added perylene in comelted samples is dissolved in the host matrix.

The exciplex The long wavelength emission observed from perylene-doped 9-CNA crystals is due to an exciplex between 9-CNA and perylene molecules. The arguments for this assignment are as follows:

a) The decay time of the emission is significantly longer (120 nsec) than that of pure 9-CNA (60 nsec) and than that of the molecular and crystal emissions of perylene.

b) The structureless emission spectrum differs from those of the two pure components.

c) The effects described in a) and b) are observed for concentrations less than 10^{-2} M/M, at which the perylene is homogeneously dissolved in the 9-CNA.

The nature of the exciplex state Evidence in favour of the charge transfer character of exciplexes has been obtained by flash photolysis experiments.[2b] These experiments have shown that the exciplex absorption contains bands which are attributable to the radical ions A^- and D^+.

The energy of the pure charge-transfer state (A^-D^+) in the gas phase, relative to that of the ground state ($A + D$), can be calculated from:

$$E(A^-D^+) = IP_D - EA_A - C \tag{1}$$

where IP_D is the ionization potential of the donor, EA_A the electron affinity of the acceptor, and C the coulomb energy which is gained when the two ions interact. It is therefore not surprising that for exciplexes in solution linear relationships have been found[19,20] between the frequency for maximum emission ν_{max} and the polarographic oxidation potential of the donor $E(D/D^+)$ and polarographic reduction potential of the acceptor $E(A^-/A)$, respectively:

$$h\nu_{\text{max}}(\text{hexane}) = E_D^{\text{ox}} - E_A^{\text{red}} - \Delta \tag{2}$$

For relatively strong acceptors and donors this relationship was found to be in good agreement[2c] with a large number of experimental data when $\Delta = 0.15 \pm 0.10$ eV. Thus the calculated ν_{max} from the polarographic literature values for oxidation of perylene[21] (+0.85 Volt) and for reduction of 9-CNA[22] (−1.7 Volt) is 19,300 ± 800 cm^{-1} which is in good agreement with the observed value (19,200 cm^{-1}).

The energy of the pure charge transfer state can be estimated according to the following expression[2c]

$$E_{CT} = E_D^{ox} - E_A^{red} + 0.32\ \text{eV} \tag{3}$$

The estimated *CT* level (23,100 cm^{-1}) is close to the 0–0 transition of perylene; it is thus obvious that for the formation of the exciplex state, terms for locally excited states (A^*D) and (AD^*) have to be introduced, in a way similar to what is known for excimers.

The geometry of the exciplex 9-CNA molecules pack in an orthorhombic[23] structure in which the molecules are arranged in columns with an interplanar distance of 3.5 Å. As discussed elsewhere[24] the marked overlap between molecules in the stack makes this structure suitable for excimer formation.

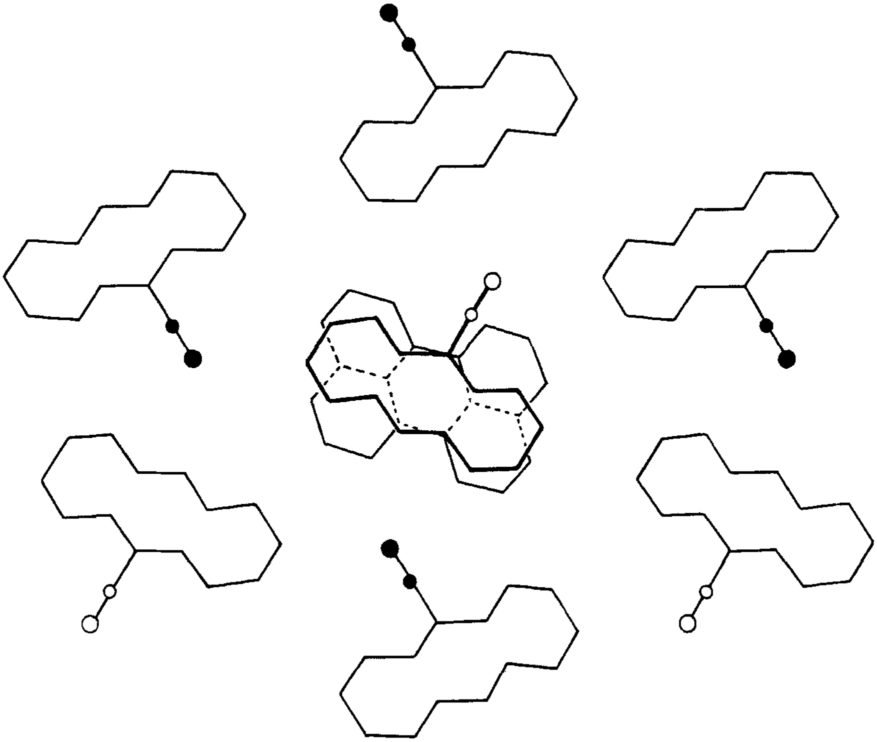


FIGURE 3 Assumed exciplex ground state geometry. The perylene and surrounding 9-CNA molecules are shown projected on a plane normal to the stack axis.

We assume that in the perylene-9-CNA solid solution perylene molecules substitute for 9-CNA ones in the host structure. Figure 3 shows the ground state geometry of a perylene molecule in a stack of 9-CNA molecules estimated on the basis of minimum repulsion with the molecules of neighbouring stacks. The resulting high 9-CNA-perylene overlap leads us to expect appreciable energy delocalisation in addition to the charge transfer as indicated also by the above calculations of the frequency of the exciplex emission.

Energy transfer The mechanism of energy transfer in excimer forming crystals has been the subject of extensive studies by various techniques.[18,25–31] It is now well established that energy transfer at the excimer exciton level is a thermally activated process. It has recently been reported[13] that in 9-CNA crystals the energy of activation for such a transfer is about 420 cm^{-1}.

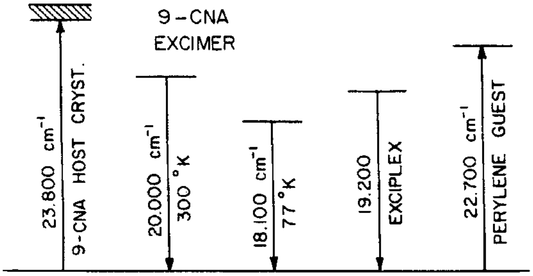
Figure 1 summarizes the effects of perylene doping on the decay time and on the shift of maxima of emission. We see that for changes of perylene concentration in the vicinity of 5×10^{-4} M/M there are sudden changes both in the decay times and in the frequency of the emission maximum. Thus energy transfer in this system is highly efficient at room temperature.

What is the mechanism for this transfer? Trivial transfer (reabsorption of fluorescence) from both monomer and excimer levels of 9-CNA host to perylene guest molecule can be ruled out since there is no detectable 9-CNA monomer emission and since the overlap between the 9-CNA excimer emission and perylene absorption is negligibly small.

From the same lack of overlap we can rule out Förster type long range energy transfer from the 9-CNA excimer to perylene. The effect of temperature, namely the freezing out of energy transfer at liquid air temperature, argues against both long range Förster type energy transfer (from either monomer or excimer to perylene) and against transfer at the 9-CNA monomer exciton. Therefore we conclude that the main channel of energy transfer is the excimer exciton and that the exciplex is formed via this transfer.

The freezing-out of energy transfer at low temperatures is common to 9-CNA as well as to other excimer-forming crystals. The slight blue shift of the emission of perylene-doped 9-CNA crystals at 77°K and the observed exciplex emission (see Figure 2, for $\lambda_{\text{exc.}} = 436$ nm) indicate that there is also no such transfer in the doped crystals.

However, since each exciplex is surrounded by molecules capable of forming excimers and yet excimers are not formed, we conclude that energy transfer does not take place even over the dimensions of a molecular pair. This is despite the fact that the exciplex emission is of higher energy than is the low temperature excimer emission (see Scheme 1).



Scheme I

Exciton diffusion parameters We can next estimate the room temperature exciton diffusion parameters using the following expression.[32,33]

$$\tau_H(0)/\tau_H(G) = 1 + K_{\text{eff}} N_G \tag{4}$$

where $\tau_H(0)$ and $\tau_H(G)$ represent decay times without and with (N_G) guest molecules respectively, and

$$K_{\text{eff}} \approx C(\{A\}) \cdot \tau_H(0)/t_H \tag{5}$$

Where t_H is the exciton hopping time from one host to another, and $\{A\}$ defining the extended trapping region. The mathematical parameter defining this phenomena is the capacity[34] $C(\{A\})$ which varies with different host–guest combinations (e.g. it is 2 for the fluorene-anthracene and 60 for the anthracene-tetracene systems[33]).

We shall approximate Eq. (5) assuming that $C(\{A\}) = 1$. This assumption is justified in part, since we treat our host 9-CNA crystal as a quasi one dimensional exciton.[23]

Evaluation of K_{eff} is based on Figure 2 and we take "half concentration" of dopant, at which $\tau_{H(0)}/\tau_{H(G)} = 2$, to be 10^{-4} M/M; at this concentration half of the excimer emission is trapped.

The K_{eff} so obtained is equal to 10^4. We have previously reported[13] that the lifetime of pure 9-CNA excimer is about 60 nsec (at 300°K), thus t_H the hopping time, will be about 10^{-11} sec^{-1}. This value is obviously a lower limit, since we have assumed that the capacity factor is equal to unity.

The corresponding one dimensional exciton diffusion constant (D_z) and length (L_z) can be estimated as follows:

$$D_z = \tfrac{1}{2}a^2/t_H \tag{6}$$

$$L_z^2 = 2D_z\tau_H(0) \tag{7}$$

where z indicates the direction along the stack axis, and a the distance between molecules along this axis. The numbers obtained from Eq. (6) and (7) are thus; $D_z = 8 \times 10^{-5}$ cm^2/sec and $L_z = 330$ Å.

Exciplex as efficient energy trap The room temperature excimer emission of pure 9-CNA is 800 cm^{-1} above the exciplex level. Despite this small energy difference ($kT \approx 200$ cm^{-1}) and the longer decay time of the exciplex compared to that of 9-CNA excimer, the exciplex state is an efficient energy sink. This is surprising at first glance since the excimer exciton is mobile and the binding energy of the 9-CNA excimer has been estimated to be $B \approx 1700$ cm^{-1}, thus the 800 cm^{-1} energy difference is not enough to explain the efficiency of the exciplex trapping.

However, this efficiency can be explained if one considers that the excimer exciton migration involves the excitation of excimer vibrational levels at the expense of the crystal phonon bath, followed by a resonative hop to a neighbouring monomer pair. It was shown that the probability[13] of such transfer from the site n to the site $n + a$ at room temperature is

$$P_{n,n+a} \alpha \exp\left[-\frac{B}{4T}\right] \tag{8}$$

where B is (approximately) the excimer binding energy.

Excimer–exciplex transfer differs from excimer-excimer transfer in one feature, that the energy of the expanded (dissociated) exciplex is lower than is the corresponding dissociated 9-CNA excimer ($\Delta E = 1100$ cm^{-1}). Thus, according to Agranovich,[35] the probability of trapping (+) and detrapping (−) can be expressed as follows:

$$R_{\pm} \alpha \exp\left[-\frac{(\Delta E \pm B)^2}{4BT}\right] \tag{9}$$

where ΔE is positive and equals the difference of 9-CNA crystal and dopant perylene absorptions (see scheme 1). It is obvious that under resonance conditions ($\Delta E = 0$) expression (8) is equivalent to (9).

On substituting $\Delta E = 1100$ cm^{-1} and $B = 1700$ cm^{-1} into (9) we find that at room temperature the rate of trapping is larger by a factor of 300 than is the rate of detrapping. This thus explains the efficiency of the exciplex as an energy sink.

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