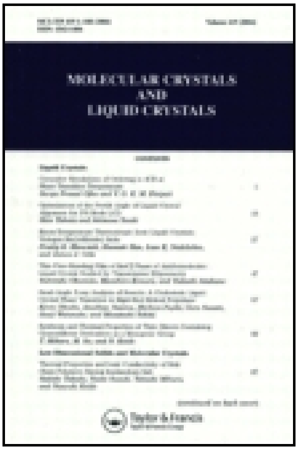

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Monomeric Films of Pyrene

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Monomeric Films of Pyrene

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Under certain conditions thin films of pyrene can be prepared which exhibit a purely monomer-like fluorescence. This fluorescence is investigated, as well as the migration of the excitation energy through the film which leads to the sensitized fluorescence of certain guest molecules which are dissolved in the film. The influence of the shape of these molecules on the energy transfer is shown.

INTRODUCTION

The crystalline structure of pyrene is well known and its fluorescence has been the subject of various investigations. In all cases was the fluorescence found to originate from the excimer of pyrene, as a result of the fact that each lattice site is occupied by a practically parallel pair of pyrene molecules. These pairs, though only weakly interacting in the ground state, as can be seen by the similarity between the absorption spectrum of the crystal and that of pyrene in solution form readily an excimer upon excitation of one of the partners. Stevens[1] summarized very lucidly the relation between the molecular structure and luminescence properties of aromatic crystals. Solid 3,4-benzpyrene was found to exhibit an excimer fluorescence spectrum as well as a monomer-like spectrum depending on the mode of preparation and the resulting crystalline structure.

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Also perylene shows this feature[2]. Recently Ern et al.(3) reported a further case of polymorphism for 4,5-iminophenanthrene, which results in the appearance of a monomer and excimer spectrum.

PREPARATION AND FEATURES OF MONOMERIC FILMS OF PYRENE

We have found that thin films of pyrene can be obtained which exhibit a structured fluorescence spectrum in the wavelenght region of the monomer emission (Figure 1). These layers can be prepared by pouring 1cc of a solution of 0.2 g/l of pyrene in ether on a clean disc of quartz (many other substrates will do) and slow evaporation of the solvent. Homogeneous and translucent layers are formed at ambient temperatures below 15°C while the disc is kept at a temperature which is 2–3°C higher. For concentrations above 0.4 g/l, or temperatures above 30°C insert: or fast evaporation of the solvent, the layers obtained showed the well known purely excimeric spectrum of pyrene. Films performed by sublimation (however fast) were exceptionless excimeric.

The material used was of high purity (Ultrapure Organic Reagents, Prinz Quality, from Organic Princeton Co.) The behavior of the films is the same when they are prepared in an oxygen free or oxygen saturated atmosphere. This is not so for excimeric crystals[4]. Also the fluorescence behavior of a film dissolved in cyclohexane is the same as that of a fresh solution.

For the following reasons we believe these films to consist of well ordered arrays of pyrene molecules and not of an amorphous conglomerate: 1. There are preliminary x-ray measurements which indicate this. 2. It will be shown that a transfer of excitation energy from pyrene to suitable solutes takes place in these films, with an efficiency that is found only in crystals. 3. The fluorescence of certain acceptors (e.g. perylene, coronene) is high polarized.

It is perhaps noteworthy that the monomeric films could be kept for a long period of time without any observable change in their emission. Scratching of the films, however, (which means, apparently, removal from the substrate) causes an immediate transformation into the excimer form, with regard to the emission spectrum. Analoglous changes have been observed by Ern et al.[3] for 4,5-iminophenanthrene.

COMPARISON BETWEEN THE MONOMERIC EMISSION OF THE FILM AND THAT OF PYRENE IN SOLUTION

The decay time of the monomer-like fluorescence of the film is 52 nsec. For the monomer emission of pyrene in solution at low concentration we found a decay time of 440 nsec. (Birks et al.[5] give a value of 445 nsec). The fluorescence

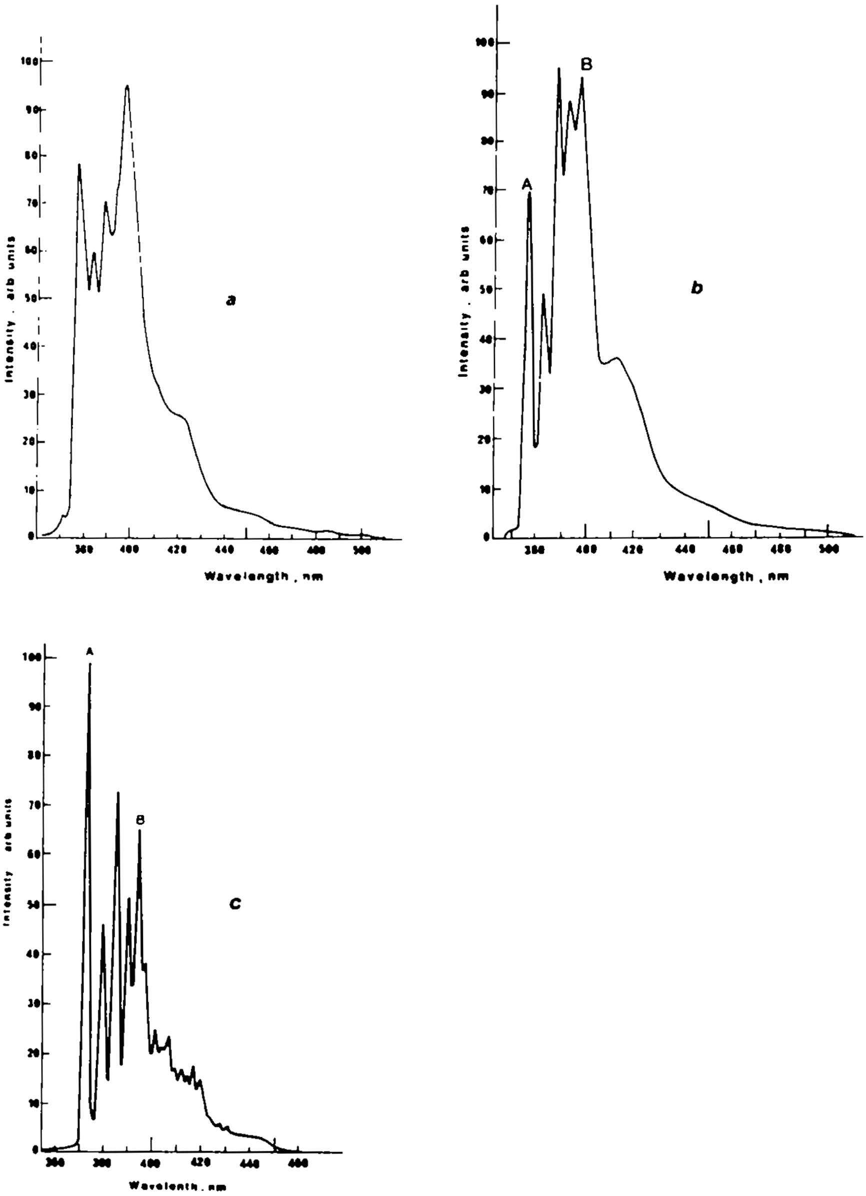

FIGURE 1 a: Fluorescence spectrum of monomeric film of pyrene, Room temperature. b: Same for 77° K. c: Fluorescence spectrum of 2 x 10^{-3} g/l pyrene in ether at 77°K.

quantum yield of the film is 0.43, that of pyrene in cyclohexane is 0.65[4]. The rate constants for radiative (k_f) and non-radiative (k_q) deactivation of the first excited level of the molecules in solution (cyclohexane) and in the monomeric film at room temperature which result from these values are (in units of $10^6 \sec^{-1}$):

	k_f	k_q
Solution	1.45	0.77
Film	8.2	11.0

The significantly higher rate constants for the film as compared with those for the solution can be related to differences in the energy levels of the two systems. Figure 2a shows the energy level diagram of pyrene in ether[6]. The transition from the ground state to the first excited state ($^1A_g \longrightarrow {}^1L_b$) is directed along the short axis of the molecule and is symmetry forbidden. Closely above the ^1L_b level lies the ^1L_a Level from which the transition to the ground state is not only allowed but is indeed very strong, as can be inferred from the absorption coefficient at the maximum of this band which is 55,000 cm^2/mole. The absorption spectrum of crystalline pyrene has been reported by several authors[7-9] The ^1L_b level is red shifted by 225 cm^{-1} with regard to the same level of pyrene in solution, whereas the red shift of ^1L_a level amounts to 1730 cm^{-1} The energy gap of 3000 cm^{-1} between the first two excited levels of pyrene in solution is thus reduced to 1495 cm^{-1} in the crystal (Figure 2b). We assume the intermolecular interactions which lead to these shifts to be of the same order in the monomeric pyrene films and in the regular crystals of pyrene. These interactions lead to an increased mixing of the first two excited levels[7,9] and the transition from S_1 to S_0 which is highly forbidden for pyrene in solution is

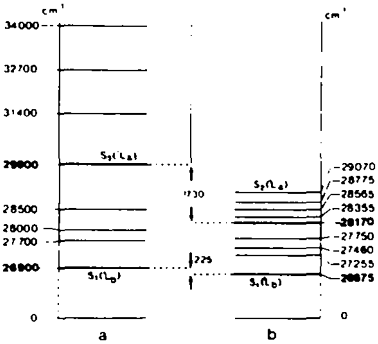

FIGURE 2 a: Energy level scheme of pyrene in ether[6]. b: Same for crystalline pyrene[9].

enhanced in the crystal. Hence, the greater rate constants which are obtained for the film.

The vibrational structure of the emission spectrum which is partly unresolved at room temperature (Figure 1a) becomes quite distinct upon cooling of the system (Figure 1b). The fluorescence spectrum of pyrene in ethanol at 90°K has been studied by Wolf.[10] For pyrene in ether at 77°K the results are shown in Figure 1c. The first five peaks (A to B) are spaced at energy intervals of 300 – 400 cm^{-1}. The next group of bands is more closely spaced. The fluorescence spectrum of the monomeric film at 77°K (Figure 1b) is rather similar to that of pyrene in ether, except for the lower intensity of the 0-0 transition (peak A) which is due to self-absorption, and the much poorer resolution at the lower energy part of the spectrum. The positions of the band heads A and B are shifted by 250 and 220 cm^{-1} which corresponds well, within the limits of accuracy, with the red shift of the first electronic level in the crystal. relative to that of pyrene in solution. We conclude thus that although the vibrational manifold of the excited electronic level appears significantly modified by the crystalline field (Figure 2), the vibrational manifold of the ground state remains rather unaffected. The difference in the transition probabilities between the monomeric film and pyrene in solution which is deduced from the different decay times is thus primarily not due to differences in the Franck-Condon factors (though these may certainly be different because of the different environment) rather than to the changed electronic transition dipole moment.

COMPARISON WITH THE MONOMERIC PART OF THE SPECTRUM OF EXCIMERIC LAYERS

In microcrystalline specimen Birks et al.[4] observed an emission band which lies at the short wavelength side of the normal excimeric crystalline pyrene emission, and they attributed this weak band to crystal defects which emit a monomer-like fluorescence. The possible mechanism which leads to this emission is the propagation of an excimer exciton toward the surface region of the film, where the trapping defects are presumably more abundant. This model is supported by the temperature dependence of the intensity of the monomer-like band of the spectrum which we observed. When the temperature is lowered enough the band disappears altogether, which means that the necessary "activation" energy for the maintenance of an excimer excition is not available and the process is halted. One may even provide an interpretation of this activation energy on the molecular level, as being related to the mutual vibration of the molecular pair at a lattice site. It is the energy which is necessary for a sufficiently wide amplitude, so that the distance of closest approach of the partners in the ground state would be equal or smaller than the greatest distance between the partners in the excited excimer state. This way, the necessary state of degeneracy between an excited and an unexcited pair is conceivably provided for an exchange interaction between the pairs to take place, which is the prerequisite for the postulated exciton motion. Klöpffer[11] and Chu et al.[12] have apparently provided enough evidence for the excimer exciton process, by observing the temperature dependence of the efficiency of energy transfer in pyrene crystals. This does still not explain the surface effect. One could, however, imagine a state of surface pairs with mutual librations of the partners†, which would lead to disintegration of the excimer into an excited and an unexcited monomer. The point which interests us most here is the fact that the monomeric part of the fluorescence of multicrystalline pyrene disappears with lowering of the temperature. The behavior of the monomeric films is drastically different, so that even at the temperature of liquid air the monomer fluorescence is fully retained. A point which is noteworthy is the equality of the decay time values for the monomer fluorescence of the excimeric crystal and that of the monomeric film. We have seen that the decay time is strongly determined by the interaction of the emitting molecule with the crystalline field, and this interaction may be similar in both cases, as has been assumed above.

ENERGY TRANSFER IN MONOMERIC PYRENE FILMS

Stevens[1] cites an earlier observation by Weigert that solid 3,4-benzpyrene does not sensitize the emission of dissolved tetracene unless this solvent has the blue-fluorescence modification for which a type-A lattice is proposed on the basis of its fluorescence spectrum. A similar situation prevails in pyrene: energy transfer to tetracene in the monomeric layer is much more efficient than in the regular excimeric crystal. It has been pointed out by Stevens[1] that the transfer efficiency is strongly dependent on the structural similarity of the host crystal and the crystalline form of the solute. This in turn is determined by the shape of the molecules (elongated molecules like anthracene and tetracene vs disc-like molecules like pyrene, perylene, coronene). We investigated the dependence of the transfer efficiency on the shape of certain solute acceptor molecules in the monomeric films of pyrene.

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† Chu et al.[12] observed a monomer-like fluorescence in multicrystalline pyrene samples at 4,2° K, whereas the emission is absent at 77° K. At 4,2° K libration of defect pairs in the bulk of the crystal may be obliviated and excimer formation prevented, thus leading to monomer emission of the originally excited molecules.

Solute: Perylene

Figure 3a shows the emission spectrum of a solid solution of 0.8 x 10^{-5} mole/mole of perylene in monomeric pyrene which has been prepared by the same procedure as the pure pyrene films (excitation wavelength 313 nm)†. The emission spectrum of perylene which is dissolved in the monomeric films resembles in its structure that of perylene in ether (Figure 3b, concentration 10^{-3} g/liter); it is, however, shifted by 900 cm^{-1} to longer wavelengths, due to the difference in the dielectric constant of the two media [14].

Before we discuss the transfer efficiency we have to state an important fact which will be treated in detail elsewhere: The intensity of the fluorescence is strongly dependent on the angle of observation, in an entirely non-Lambertian manner. The results reported below were obtained by integration of the intensities over the angles of observation between 0° and 90° at intervals of 5°.

The transfer efficiency was determined by two methods. Method a, Comparison of intensities: Let γ be a constant factor which accounts for the fraction of photon collection by the measuring system, N the number of excited donor molecules, ϵ the transfer efficiency, η_D and η_A the fluorescent quantum yields of the donor (without acceptor) and of the acceptor, respectively, I_D and I_A the

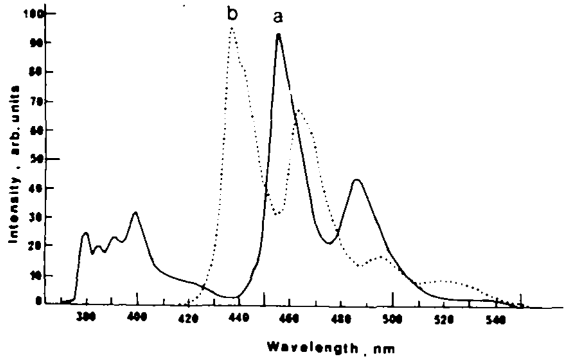

FIGURE 3 Curve a: Fluorescence spectrum of solid solution of 0.8 x 10^{-5} mole/mole of perylene in monomeric film of pyrene. Curve b: Fluorescence spectrum of 10^{-3} g/l perylene in ether.

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† Srinivasan et al. [13] report an emission spectrum which is quite similar to that of Figure 3a for wavelengths longer than 430 nm which they observed when pyrene at low concentrations was dissolved in biphenyl. This structured emission spectrum they attribute to an excimer species which decays into the vibrational manifold of the monomer. Since pyrene contains very often perylene as an impurity their spectrum could perhaps be that of perylene in a monomeric arrangement of pyrene. This is more likely so, since the structured spectrum appears on a strong background of pyrene monomer fluorescence.

measured intensities of the donor and acceptor, respectively, then the following relations hold:

$$I_{D'} = \gamma N_0 (1-\epsilon) \eta_D \qquad I_A = \gamma N_0 \epsilon \eta_A$$

$$\epsilon = \frac{\alpha}{\alpha + \beta} \quad \text{where } \alpha = \frac{I_A}{I_{D'}} \qquad \text{and} \quad \beta = \frac{\eta_A}{\eta_D} \quad .$$

This way the transfer efficiency is determined by the measurement of the donor and acceptor fluorescence of the same sample (with proper correction for the wavelength sensitivity of the photomultiplier), and artifacts due to differences in the scattering factor of different samples are avoided. With values of η_D=0.43 and η_A = 0.94 [15] the results ϵ_i given in Table 1 were obtained.

TABLE 1

Decay time of pyrene and efficiency of energy transfer from pyrene to perylene in monomeric films of pyrene. ϵ_i from intensities; ϵ_τ from decay times.

c $(\frac{\text{mole}}{\text{mole}})$	0	8×10^{-8}	2.65×10^{-7}	8×10^{-7}	2.65×10^{-6}	8×10^{-6}	8×10^{-5}	8×10^{-4}
ϵ_i		0.13		0.29		0.47	0.70	
τ (nsec)	52	45	41	38	33.5	26	16.5	9.5
ϵ_τ		0.14	0.21	0.27	0.35	0.50	0.68	0.84

Method b, Decay time measurements: The decay curves of the pyrene fluorescence for various concentrations of the acceptor were recorded (by a sampling oscilloscope in conjunction with a CAT) (for excitation at 337 nm) and the decay time was computed by deconvolution of the decay curves for the shape of the excitation pulse, assuming exponential decay of the fluorescence. The transfer efficiency is then given by the relation $\epsilon = (\tau_0 - \tau)/\tau_0$ where τ and τ_0 are the decay times of the donor fluorescence with and without the acceptor present. The results are designated by ϵ_τ in Table 1.

In evaluating these results we first note that the emission of perylene is due to energy transfer only. This is so because the optical density of perylene even at the highest concentration is only 4 x 10^{-5} and 3.4 x 10^{-5} of that of pyrene for excitation at wavelengths 337 and 313 nm, respectively. We were also unable to obtain any trace of perylene fluorescence by direct excitation in a wavelength region at which pyrene is transparent and perylene still absorbs (e.g. 436nm). There are two essentially different transfer mechanisms to be considered: A long range interaction between an excited pyrene molecule and a perylene molecule, and an excitation hopping model with subsequent short range interaction. It can easily be shown that a long range dipole-dipole interaction, according to whatever formalism, will not explain the results. For example, the transfer efficiency at the lowest concentration would correspond to a Förster radius of 400Å which is of course impossible. The Förster radius which we calculated from the overlap integral ($4.6 \times 10^{-14} cm^6 mole^{-1}$)† was found to be 22Å. Similarly high transfer efficiencies have been known long ago for other solid solutions and the problem of the mechanism involved has been treated by various authors (for references see (16)). It can also be shown that a hopping model alone with ultimate close interaction energy transfer does not fit the results at all. According to such model the quenching constant for energy transfer $Q \doteq \epsilon/(1-\epsilon)$ has been shown to obey the relation $Q = 0.66$ pnc (c is the concentration of the acceptor, n the number of hopping steps in the abscence of the acceptor, p the probability for energy transfer from an excited donor molecule to a neighbouring acceptor molecule)[17]‡. This relation implies the product pn to be a constant, which is in variance with the results. From the results of Table 1 one derives values for pn which vary from 5×10^6 to 10^4 for a change in concentration from 8×10^{-8} to 8×10^{-4} mole/mole. For a medium concentration of 8×10^{-6} some reasonable values of the diffusion parameters are obtained: The frequency of the energy jump $k = n/\tau_0$ assuming $p \approx 1$ (since energy transfer from pyrene to pyrylene is quite effective even in liquid solution[18]) is found to be $3.7 \times 10^{12} sec^{-1}$. This value is of the same order of magnitude as that for crystals of anthracene[19]. The diffusion constant $D = a^2 k/3$ (a is the lattice constant here taken as 5Å) is then $3.3 \times 10^{-3} cm^2 sec^{-1}$. The mean free path of the excition $L = (3D\tau_0)^{1/2}$ equals 0.2μ. It may be important to mention that no dependence of the decay time on the thickness of the film was observed (not so for excimer layers, see also ref. (4)). In view of the fact that all films were thinner than the calculated mean free path for energy migration this result implies that surface annihilation of the energy is not significant.

The results may conceivably be reconciled with theory in at least two different ways, which both require further elaboration. First we have to consider the combination of energy migration with subsequent long range transfer, a method tried by Powell.[20, 21]. For solutions in general such methods have been worked out by several authors (e.g. 22,23,24). We defer the treatment of these calculations. The second point which has to be considered is the strong de-

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† The absorption spectrum of perylene in the monomeric film which is required for this caculation could not be measured directly. Instead we relied on the fact, cited above, that except for the red shift, the emission spectrum of perylene in pyrene is similar to that of perylene in ether, and assumed the absorption spectrum to behave similarly.

‡ In ref. (19) as in other works p is assumed to be unity.

pendence of the diffusion length on acceptor concentration. An increase in diffusion length with decreasing acceptor concentration was found also in annealed mixed crystals of anthracene and naphthalene[25]. It is well possible that in the vicinity of an acceptor molecule, which represents a crystal defect, the propagation of the energy is perturbed. This would certainly hold for a true exciton band model. With increasing concentration this effect may lead to a drastic reduction of the whole process of energy migration. In a quite different system, the transfer efficiency was even found to decrease with increasing acceptor concentration beyond a certain range[26].

Solute: Coronene

Figure 4, curve a, shows the emission spectrum of a solid solution of 6.7 x 10^{-6} mole/mole of coronene in a monomeric film of pyrene. This emission again is solely due to energy transfer from pyrene [to coronene] to coronene. Before we consider the transfer efficiency we point to the fact that the fluorescence spectrum of coronene in the film is quite different from that of coronene in ether (at 0.02 g/l)(curve b). This was not so in the case of perylene and is also not the case for tetracene as solute. We remember that the fluorescence decay time of the monomeric film differs considerably from that of pyrene in liquid solution. Also for coronene (excited via energy transfer) the decay time is greatly reduced in the film as compared to that for coronene in ether (140 vs 360 nsec). Again we deal with a $S_1 \rightarrow S_0(^1L_b \rightarrow {}^1A_g)$ transition which may be considerably enhanced

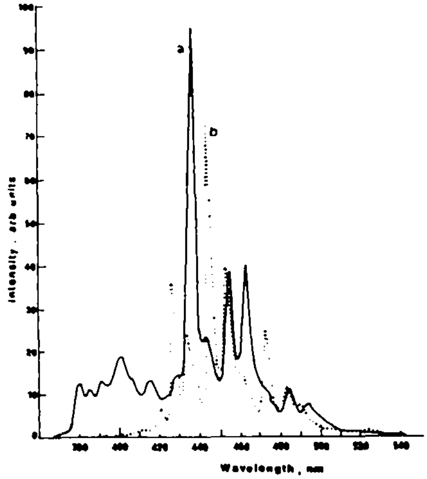

FIGURE 4 Curve a: Fluorescence spectrum of solid solution of 6.7 x 10^{-4} mole/mole coronene in monomeric film of pyrene. Curve b: Fluorescence spectrum of 2 x 10^{-2} g/l coronene in ether.

by mixing with the S_2 state. The generalization of this effect for weak transitions to the ground state is certainly worth consideration. Also the considerably different vibrational structure of the spectrum may result from a strong influence of the crystalline field on the selection of the transitions to the ground state. (The identical polarization throughout the fluorescence spectrum excludes transitions from different states).

TABLE 2

Efficiency of energy transfer from pyrene to coronene in solid solutions of coronene in monomeric films of pyrene

c mole/mole	6.7×10^{-6}	6.7×10^{-4}	6.7×10^{-4}	6.7×10^{-3}
ϵ	0.24	0.56	0.77	0.92
pn	7.1×10^{4}	3.4×10^{4}	0.8×10^{4}	0.3×10^{4}

The transfer efficiency ϵ for various concentrations of coronene (assuming a quantum yield of 0.28[27]) is given in Table 2. The table also includes values for pn which has been defined above. Comparison of these values with those of Table 1 shows that for low concentrations energy transfer to coronene is considerably less efficient than to perylene. At higher concentrations the transfer efficiencies are similar. It is also noted that the variation in the pn-values is much smaller than for perylene. From this we conclude again that in the case of perylene the transfer efficiency at low concentrations is strongly determined by a long range transfer mechanism which is assisted by energy migration through the crystal, while at higher concentrations the strength of the long-range interaction is less critical. The difference between perylene and coronene in the strength of the interaction is readily explained by the difference in the overlap integral of the donor fluorescence and acceptor absorption, which for coronene equals 4.9×10^{-16} cm^{6}mole^{-1} and is thus by two orders of magnitude smaller than for perylene. Also because of the greater similarity in molecular shape between pyrene and perylene as compared with coronene, a perylene molecule will orient itself closer to the position of a pyrene molecule which it replaces than does a molecule of coronene. These orientational relations between the interacting molecules may significantly affect the probability for energy transfer. We assumed for perylene a close-interaction probability of one. Relative to this value the probability for transfer to coronene is found to be 0.36 (from comparison of the pn-values for medium concentrations of perylene and coronene).

It shall be noted that energy transfer to coronene in the monomeric film is much more efficient than in the excimeric crystal. This is so because of the much faster exciton motion in the former than in the latter[11, 12].

Solute: Tetracene

For perylene and coronene as solutes homogeneous films were obtained, which means that only the pyrene monomer and acceptor fluorescence were observed and that the ratio of intensities of the two emissions was quite constant over the whole area of the film. With tetracene as solute the homogeneity depends strongly on the concentration. Homogeneous samples could be obtained only for concentrations below 10^{-4} mole/mole. For higher concentrations the ratio of intensities of the donor and acceptor fluorescence varied over the film and with increasing concentration an increasing portion of the film exhibits the excimer fluorescence of pyrene. These features indicate an inhomogeneous distribution of tetracene molecules in the film. Those portions of the film which contain a small concentration of tetracene are still monomeric while those with a higher content of tetracene grow in the excimeric form of pyrene. The differences in the influence of the solutes on the crystalline structure is readily understood by their different shapes. Thus while perylene and coronene which have a disc-like shape do not disturb the formation of the less stable monomeric films, tetracene with its rod-like shape interferes with the balance of forces (including those with the substrate) which makes the structure possible. (Also naphthalene as solute was found to interfere with the formation of monomeric films).

TABLE 3

Efficiency of energy transfer from pyrene to tetracene in solid solution of tetracene in monomeric films of pyrene

c mole/mole	8.85×10^{-6}	8.85×10^{-5}	8.85×10^{-4}
ϵ	0.18	0.41	0.70
pn	3.76×10^{4}	1.18×10^{4}	0.44×10^{4}

Table 3 shows the transfer efficiency as a function of concentration. For concentrations above 10^{-4} mole/mole the transfer efficiency is comparable to that for perylene and coronene, for lower concentrations it is much smaller although the overlap integral for tetracene is greater than that for coronene by an order of magnitude (6.2×10^{-15} vs $4.9 \times 10^{-16}\,\mathrm{cm}^6\,\mathrm{mole}^{-1}$). This reduction in transfer efficiency is again due to reduced energy migration and/or to an unfavorable orientational factor. The different arrangement of tetracene as solute in the film can also be seen by the fact that its fluorescence is not polarized and that the intensity depends only weakly on the angle of observation, in contrast to the behaviour of perylene.

Solutes: 1,6-Diphenyl-1,3,5-hexatriene (DPH) and 1,8-diphenyl-1,3,5,7 octatetraene (DPO)

For an orginal concentration of 10^{-3} mole/mole of DPH a very weak fluorescence of the solute was observed, although the quantum yield of DPH in liquid solution is rather high and the overlap integral for this solute (1.2×10^{-14} cm^{6}mole^{-1}) is over 20 times greater than that for coronene. It appears thus that energy transfer to DPH in the monomeric film is negligible.

For DPO even at a concentration of 10^{-2} mole/mole no fluorescence of the solute could be detected. The overlap integral for this solute (8.6×10^{-14} cm^6 mole^{-1}) is over two orders of magnitude greater than that for coronene and its value is in fact greater than that for any other solute considered here.

These molecules are rather long as compared to perylene and coronene and the reason for the abscence of energy transfer to them is most probably that they are not dissolved in the film. In contrast to the behavior of tetracene and naphthalene which by their dissolution cause the breakdown of the monomeric structure, these solutes do not enter the film, and thus the fluorescence of pyrene appears again purely monomeric. This does however, not explain why these molecules are not sensitized by energy migration to the surface. The total absence of any fluorescence of DPO may thus perhaps indicate a directional flow of the excitation energy along certain crystalline planes of the film which coincide with the plane of the substrate.

Generalizing we summarize that with regard to energy transfer the guest molecules can be divided into three categories:

1) Molecules whose shape is similar to that of the molecules of the host film which even at high concentrations form true solutions. Their orientation in the film tends to be close to that of the host molecules. Energy transfer to these molecules is very efficient even at very low concentrations.

2) Molecules whose dimensions are not too different from those of the host molecules but whose shape is significantly different. Their orientation in the host crystal is different from that of the host molecules and is perhaps random. Their presence at high concentration interferes with the formation of the structure of the monomeric films. Energy transfer to these molecules at low concentrations is not efficient.

3) Molecules whose dimensions are considerably greater than those of the host molecules. Their presence, even at high concentrations does not perturb the formation of the monomeric film because they do not form a true solid solution. Energy transfer to them is negligible even at high concentrations.

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