Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Monomer Emission from Excimer Forming Crystals: Pyrene and Perylene

Nori Y. C. Chu [a] & David R. Kearns [a]

[a] Department of Chemistry, University of California, Riverside, Calif, 92502

Version of record first published: 28 Mar 2007.

To cite this article: Nori Y. C. Chu & David R. Kearns (1972): Monomer Emission from Excimer Forming Crystals: Pyrene and Perylene, Molecular Crystals and Liquid Crystals, 16:1-2, 61-74

To link to this article: http://dx.doi.org/10.1080/15421407208083580

Molecular Crystals and Liquid Crystals. 1972. Vol. 16, pp. 61–74

Printed in Great Britain

Monomer Emission from Excimer Forming Crystals: Pyrene and Perylene

NORI Y. C. CHU† and DAVID R. KEARNS‡

Department of Chemistry
University of California
Riverside, Calif. 92502

Received May 12, 1971

Abstract—The phenomenon of monomer emission from excimer forming crystals has been investigated for pyrene and perylene. A variety of spectroscopic techniques have been used to demonstrate that genuine monomer emission can be observed from pyrene crystals. The emitting monomers appear to be located in disordered regions of the crystal situated within 5×10^2 nm of the surface. Both delayed monomer and excimer emission have been observed at 4.2 °K and information on the range of the monomer exciton migration has been obtained. The low temperature emission observed from the dimeric α-form of perylene crystals appears to be either from highly perturbed perylene monomers located in disordered regions of the crystal or from impurities. The unusual temperature dependence previously observed for the emission spectrum of the monomeric β-form of perylene crystals is shown to be due largely to reabsorption effects.

1. Introduction

There are a number of aromatic hydrocarbons which crystallize as coplanar sandwich dimers (B-type crystals in Stevens' classification)(1) and consequently yield only structureless excimer type emission spectra under most conditions. Two crystals which fall into this category are pyrene and the α-form of perylene. Under certain special conditions, however, the emission from even these crystals has shown a structure characteristic of monomers in addition to excimer emission.(2,3) In order to account for the simultaneous appearance of " monomer " and excimer emission (Processes 1 and 2, Fig. 1) from the same crystal, Tanaka proposed a potential energy diagram similar to the one shown in Fig. 1 to describe the intermolecular interaction between planar pairs of molecules in the

---

† U.S. Public Health Service Postdoctoral Fellow, 1967–70.

‡ John Simon Guggenheim Fellow, 1969–70.

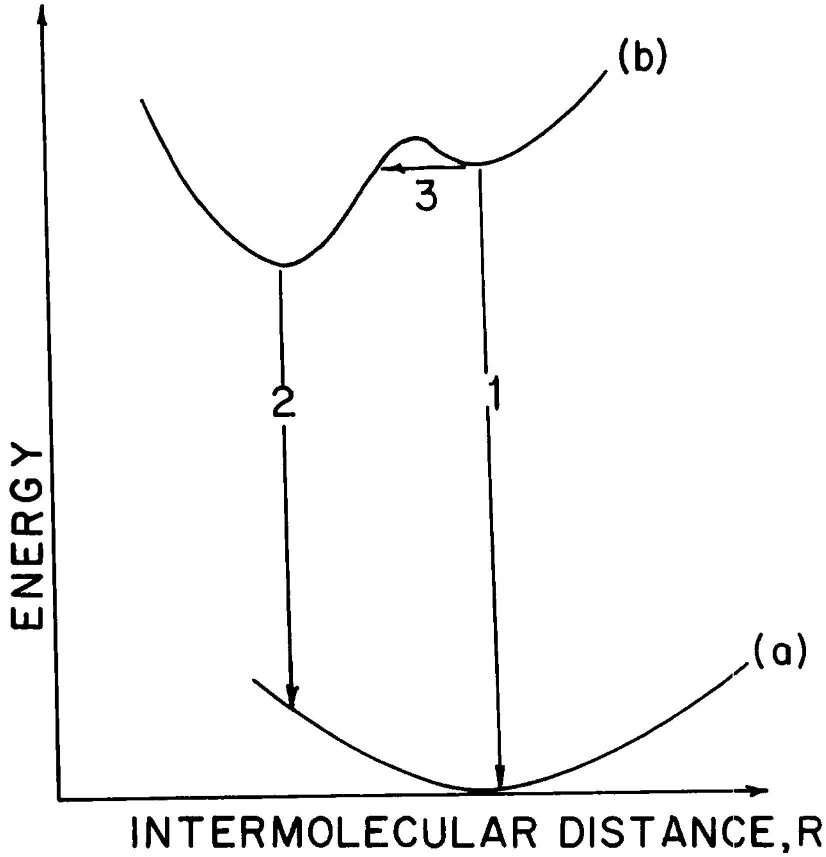

Figure 1. Potential energy diagram representing the interaction of a sandwich pair of molecules in a crystal with (a) both molecules in their ground states; (b) one molecule in its first excited state.

crystal.(3) The essential feature of this diagram is the appearance of the barrier to excimer formation in the excited state potential energy curve. If this barrier were sufficiently large, it is easy to understand that excimer formation (Process 3) would be prevented at low temperatures. At higher temperatures, however, the barrier could be surmounted during the lifetime of the monomer and only excimer emission would be observed. At intermediate temperatures both monomer and excimer emission could be observed.

While this provides a plausible explanation for the appearance of monomer emission at low temperatures, other alternatives do not appear to have been ruled out. Furthermore, certain testable aspects of Tanaka's proposal do not appear to have been checked. Finally positive identification of the monomer emission from these crystals remains to be achieved. In order to clarify this somewhat unsatisfactory situation we have reinvestigated the phenomenon of " monomer " emission from two B-type molecular crystals—pyrene and the α form of perylene.

2. Experimental

Pyrene obtained from Matheson, Coleman and Bell Company was purified as previously described.(4) Thin film pyrene samples were prepared by evaporation of a small amount of dilute benzene solutions of pyrene between two glass plates. Perylene (99 + %) obtained from Aldrich was first vacuum sublimed before crystal growing. Both the α-form and β-form perylene crystals were grown from benzene solution in the absence of oxygen in order to prevent oxidation and then separated manually.

Fluorescence emission and excitation spectra were measured by a standard fluorimeter with appropriate Corning or interference filters.(4) The delayed fluorescence of pyrene was measured by using a phosphorimeter. Fluorescence decay lifetimes were measured by an apparatus using single photon counting techniques as described in an earlier publication.(4)

3. Results and Discussion

3.1. PYRENE

The emission spectrum of a thin film *microcrystalline* pyrene sample is illustrated in Fig. 2 for temperatures ranging from 342 °K to 4.2 °K. At 77 °K the emission spectrum shows only the characteristic broad, structureless pyrene excimer emission. However, at higher or lower temperatures an additional anomalous, partially structured emission appears at higher energies than the origin of the excimer emission. A very similar room temperature spectrum has previously been reported by Birks and Cameron(2) and recently by Klöpffer and Bauser.(5) At 4.2 °K the intensity of this anomalous emission is even larger than that of excimer emission by about a factor

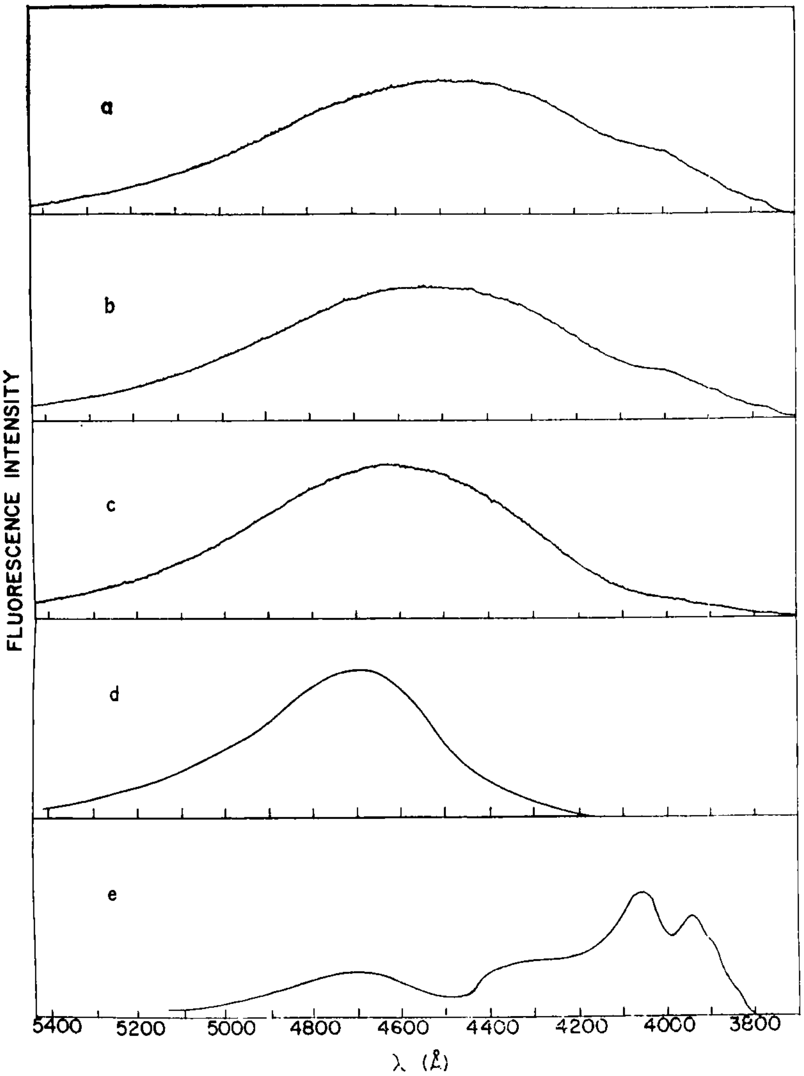

Figure 2. Fluorescence spectrum of a thin film microcrystalline pyrene sample at: (a) 342°K, (b) 295°K, (c) 200°K, (d) 77°K, (e) 4.2°K.

of 4. The emission spectrum at 1.9 °K is essentially identical to that at 4.2 °K. In a *multicrystalline* pyrene crystal the intensity of this anomalous emission is only about 5–10% that of the excimer emission at 4.2 °K, and in good single crystals no anomalous emission is observed.⁽⁶⁾

When the 4.2 °K excitation spectrum of a thin film pyrene sample is monitored at the maximum of the anomalous emission (410 nm) or at the maximum of the excimer emission (470 nm) the results shown in Fig. 3 are obtained. It should be noted that even the thin film pyrene sample is optically fairly thick and this is demonstrated by the excimer excitation spectrum which shows complete absorption at 378 nm. In spite of this fact, the excitation spectrum of the anomalous emission monitored at 410 nm shows considerable structure and is essentially identical to the absorption spectrum of an optically thin pyrene crystal.⁽⁷⁾

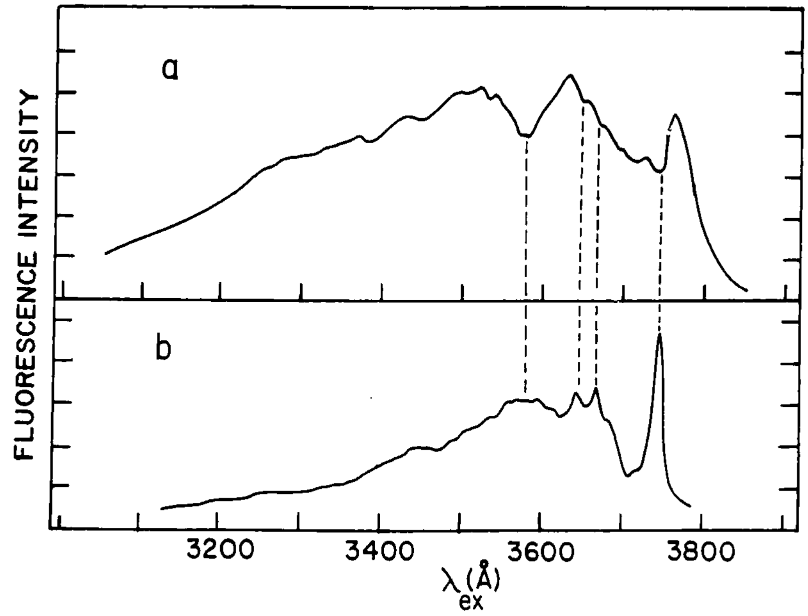

Figure 3. Fluorescence excitation spectrum of a thin film microcrystalline pyrene sample at 4.2 °K monitored at (a) the peak of the excimer emission (470 nm); (b) the peak of the perturbed monomer emission (410 nm).

Thin film pyrene samples at 4.2 °K also exhibit a weak delayed fluorescence (see Fig. 4) and it is interesting to note that the ratio of the intensity of the delayed excimer emission to the delayed monomer emission of the delayed fluorescence is $\sim 4:1$ whereas in the prompt emission spectrum the monomer emission is ~ 4 times stronger than the excimer emission. The decay of the delayed fluorescence is in the milisecond region and no evidence for phosphorescence has been observed.

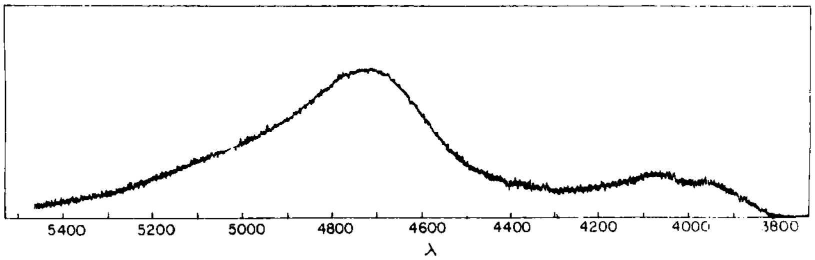

Figure 4. Delayed fluorescence spectrum of a thin film microcrystalline pyrene sample at 4.2 °K.

After considering various possible interpretations, we have concluded that the anomalous high energy emission bands originate from perturbed pyrene monomers which are located in a disordered region near the surface of the crystal. The basis for this assignment is as follows:

(i) Spectral Distribution: The spectral distribution of the anomalous emission is quite similar to the emission spectrum of monomeric pyrene, although it is more diffuse and red shifted from the emission spectrum of monomeric pyrene in methylcyclohexane glasses at 77 °K (see Fig. 5).

(ii) Lifetime: The decay of the anomalous emission is exponential with a lifetime of 323 nsec which should be compared to pyrene fluorescence lifetimes of 287 nsec in polystyrene and 295 nsec in PMMA at room temperature.(8) There are relatively few organic molecules which have lifetimes in this range, and consequently this is supporting evidence that the emitting molecules are, in fact, pyrene monomers.

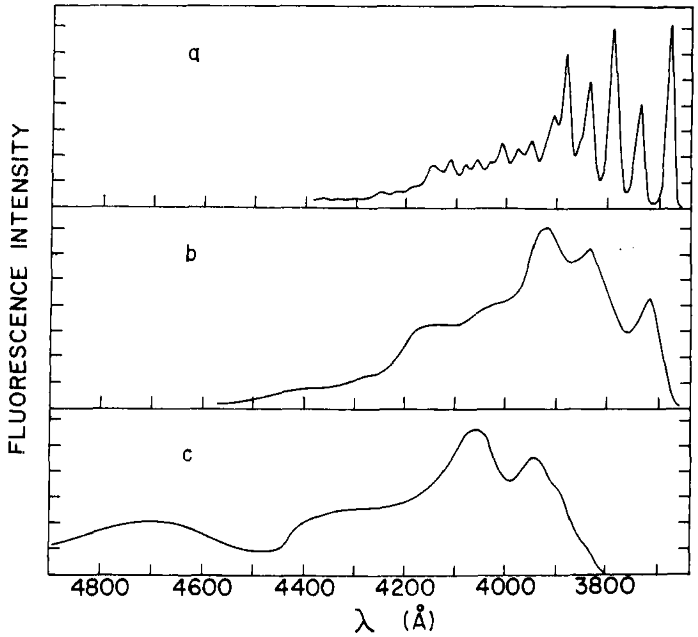

Figure 5. Fluorescence spectrum of pyrene in methylcyclohexane glass at 77 °K: (a) under moderate resolution conditions; (b) under low resolution conditions; (c) fluorescence spectrum of a thin film pyrene sample at 4.2 °K.

(iii) Relative Intensity of Excimer and Monomer Emission: With bulk *polycrystalline* samples the intensity of the monomer emission relative to the excimer emission varies from about 0.05 to 0.1 at 4.2 °K depending upon how the sample is cooled. With thin film samples, however, the intensity of the perturbed monomer emission is even larger than the excimer emission (see Fig. 2). These variations in the relative intensities of the monomer and excimer emission provide additional evidence against assigning the anomalous emission to impurity emission, since doping experiments described elsewhere indicate that the impurity level would have to approach 5×10^{-3} mole/mole in order to account for the intensity of the monomer emission.(4) Such an impurity concentration is not consistent with the lifetime measurements (112 ± 2 nsec at 295 °K) which indicate that the crystals are in fact quite pure. Since the monomer emission is in competition with excimer emission, this interpretation also accounts for why the excitation spectrum of the excimer emission shows minima at those wavelengths (375, 367 and 364 nm) where the monomer excitation spectrum exhibits maxima.

The excitation spectrum of the monomer emission (shown in Fig. 3) clearly demonstrates that the emitting monomers are located near (within an extinction depth at 375 nm) the surface of the crystal. Thick crystals, and even the thin film sample which we prepared, were completely opaque at wavelength shorter than 378 nm and, therefore, if the emission were from special monomer sites located *within* the bulk of the crystal, the monomer excitation spectrum should have been the same as the excitation spectrum of the excimer emission. Instead, we find that the monomer excitation spectrum exhibits considerable fine structure, and is essentially identical to the absorption of an optically thin crystal. The implication from this result is that light which is absorbed nearest to the crystal surface is most effective in generating the monomer emission. The observation that the intensity of the monomer emission relative to the excimer emission increases when the sample thickness is decreased, provides a further indication that the emission is from perturbed pyrene monomers located very near the surface of the crystal. These perturbed pyrene monomers cannot, however, be located right at the surface of the crystal since the intensity of the emission is not reduced when the surface of crystal is coated with a film of potassium iodide.

The experiments described above also permit us to draw certain conclusions regarding energy transfer in pyrene crystals at 4.2 °K. From the excitation spectra we may conclude the range of energy transfer at the *monomer* exciton level is on the order of the extinction depth at 375 nm, or $\sim 5 \times 10^2$ nm. If the range were significantly larger than this length, the monomer excitation spectrum would have more nearly resembled the excimer excitation spectrum. On the other hand, if the range was significantly less than 5×10^2 nm, it would be difficult to account for the relatively high intensity of the monomer emission as compared to the excimer emission. The range of the monomer exciton derived from these experiments is in reasonable agreement with the range (> 30 nm) which we previously deduced from an investigation of the quenching of pyrene emission in doped crystals.(4)

The fact that the emitting monomers are confined to a region of the crystal near the surface indicates that Tanaka's explanation(3) for the appearance of the monomer emission is not applicable in the specific case of pyrene. If a barrier in the normal excited potential energy curve were responsible for this effect, then the appearance of monomer emission should have been a bulk effect, rather than a " surface " effect as observed here.

The temperature dependence of the monomer emission is rather interesting. As illustrated in Fig. 2, the perturbed monomer emission disappears at 77 °K but reappears again at 195 °K and continues to increase as the temperature is raised. To account for this temperature dependence of the monomer emission we suggest the following explanation. At 4.2 °K the specially perturbed monomers which are located in disordered regions of the crystal function as shallow traps of monomer excitons. Since these traps are presumably located in disordered regions of the crystal, this explains why they are not quenched by excimer formation as would be expected if they were located in the ordered regions of the crystals. At sufficiently high temperatures, $\sim$ 77 °K, these shallow trapping centers become depopulated during the long lifetime of the excited monomer, and the excitation energy can be transferred back into the bulk of the crystal where it is trapped by excimer formation. This accounts then for the disappearance of the monomer emission and of the minima at 375, 367 and 364 nm in the *excimer* excitation spectrum at 77 °K. At still higher temperatures where we have shown that " excimer exciton " migration becomes more efficient(4) a thermally activated transfer of energy back to perturbed monomers becomes possible. Depending upon the equilibrium distribution of excitation energy between monomers and excimers, some monomer emission can be observed. Judging from intensity of the excimer and relative to the perturbed monomer emission at room temperature, the excimer state should be located about 24,500 cm^{-1} above the ground state, or about 2,100 cm^{-1} below the monomer state.

The observation of delayed fluorescence of pyrene crystals at 4.2 °K indicates that the monomer triplet exciton is mobile. Since singlet *excimer* exciton migration is already negligible by 77 °K, this would argue against the formation of triplet excimers which we would expect to be similarly immobile at temperatures below 77 °K.

The theoretical studies by Chandra and Lim⁽⁹⁾ and the experimental work of Chandross and Dempster⁽¹⁰⁾ also support the notion that triplet excimers are unstable with respect to dissociation into a triplet monomer and a ground state molecule.

3.2. PERYLENE

Perylene has two different crystal forms: the α-form which has a dimeric structure, and the β-form which is monomeric and similar to the crystal structure of naphthalene and anthracene.⁽³⁾ As might be expected, the α-form of perylene shows a broad structureless emission at 295 and 77 °K (see Fig. 6). When this crystal is cooled to 4.2 °K however, the emission spectrum develops some structure with peaks appearing at 502, 532 and 573 nm, as illustrated in Fig. 6. Entirely similar results were previously reported by Tanaka.⁽³⁾ Although this might appear to be another case in which monomer emission is appearing at low temperatures along with the excimer

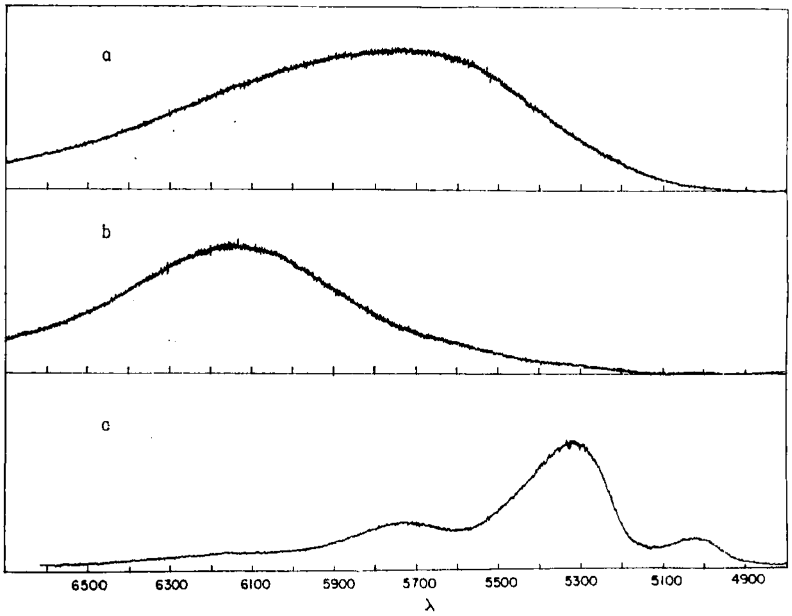

Figure 6. Fluorescence spectrum of the dimeric α-form perylene crystal at (a) 295 °K; (b) 77 °K; (c) 4.2 °K.

emission, the following pieces of experimental data make such an assignment questionable. The excitation spectrum of the α-form of perylene given in Fig. 7 shows two small peaks at 492 and 481 nm on the long wavelength side of the strong perylene absorption, but these peaks are absent in the direct absorption spectra of thick perylene crystals.(11) Furthermore, the crystal emission spectrum is more red shifted when it is excited at 480 nm than when it is excited at either 436 or 366 nm. We can only conclude from these observations that the emission which we have observed from α-perylene crystals is either from impurities which have been sensitized by energy transfer from perylene or possibly from highly perturbed monomers located in disordered regions of the crystal. Since the emission spectra reported by Tanaka(3) for the α-form of perylene are entirely similar to ours, it would appear that he too was observing impurity emission.

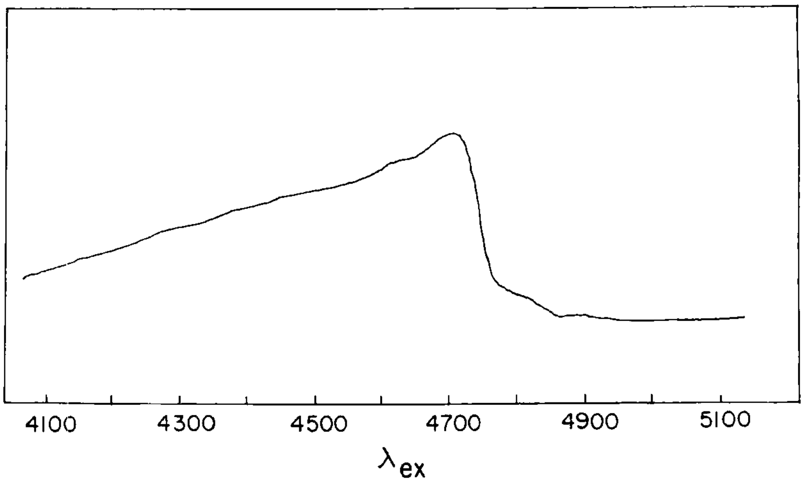

Figure 7. Fluorescence excitation spectrum of the dimeric α-form perylene crystal at 4.2 °K. The constant intensity between 4800–5100 is due to stray light.

Because of the strength of the ${}^1A \rightarrow {}^1L_A$ transition some precaution must be taken in order to minimize reabsorption effects. By masking the edges of the crystal, and by carrying out front excitation the reabsorption effects can be minimized and the spectrum shown in

Fig. 8 is obtained. In this spectrum, peaks are clearly evident at 490, 520 and 559 nm. Upon cooling the emission becomes even more structured as demonstrated in Fig. 9. The data in Fig. 8 clearly indicate that reabsorption effects can be quite serious with β-form perylene, and this could be the reason why the 295 °K emission spectra reported by Tanaka lack the first emission peak at 490 nm.(3) Since reabsorptions effects are reduced by reducing temperature, this would account for the appearance of the 490 nm peak at 77 °K in Tanaka's spectrum and its further resolution into three separate peaks at 4.2 °K (Fig. 9). Comparison of the relative intensities of the bands at 540 nm and at 490–500 nm region measured by Tanaka and by us clearly indicates that the 4.2 °K emission spectrum measured by Tanaka still shows some degree of reabsorption. Tanaka had suggested that the first three emission peaks centered at 500 nm arise from surface state emission; however, our measurements indicate that these are just part of the normal emission spectrum. Consequently, it is not necessary to invoke surface state emission to account for the low temperature emission spectrum of β-form perylene.

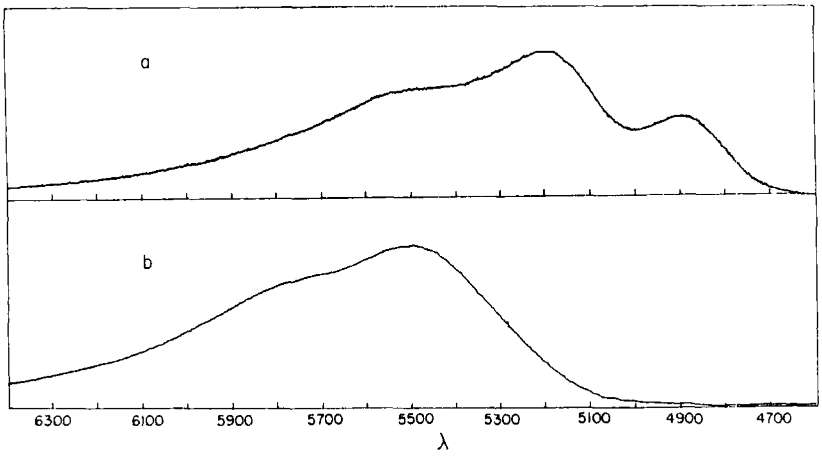

Figure 8. Fluorescence spectrum of a monomeric β-form perylene single crystal at 295 °K: (a) front surface excitation; (b) illumination and emission are perpendicular to emphasize reabsorption effect.

4. Summary

The studies which we have presented here demonstrate that it is possible to observe genuine monomer emission from pyrene crystals. At the same time, these observations indicate that the occurrence of monomer emission in these crystals is related to the formation of disordered regions in the crystals, and that it is not a normal property of carefully grown regular crystals. Thus, the possibility that the molecular motion needed to form excimers could be frozen out is not realized in the case of pyrene. Our results indicate that the structured emission from the dimer crystalline form of perylene at low temperatures is either due to impurities, or to special highly perturbed monomers which again are probably located in disordered regions of the crystal. It would appear then, that perylene and pyrene are not cases where excimer formation in the bulk of an unperturbed crystal can be frozen out at low temperatures.

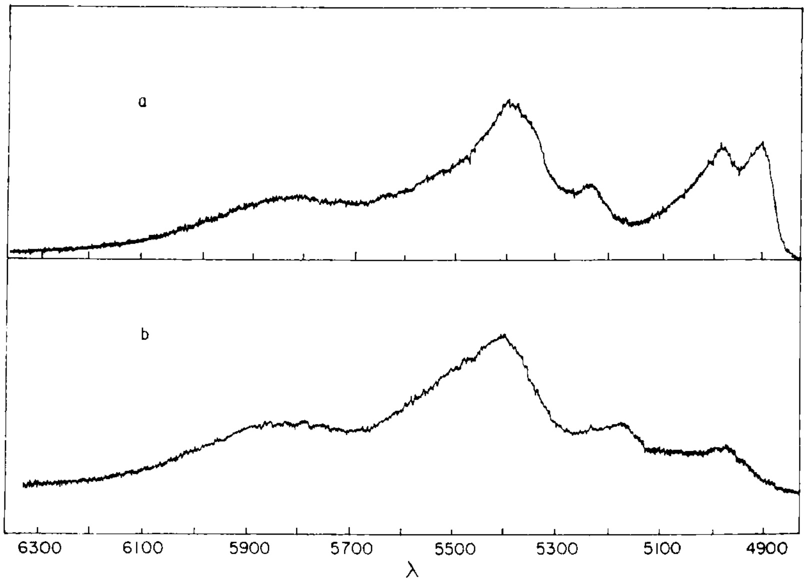

Figure 9. Fluorescence spectrum of monomeric β-form perylene crystals at (a) 4.2 °K and (b) 77 °K by front surface excitation.

Acknowledgements

The support of the National Science Foundation (Grant No. GP–12050), the John Simon Guggenheim Foundation, and the U.S. Public Health Service is most gratefully acknowledged.

REFERENCES

1. Stevens, B., *Spectrochim Acta* **18**, 439 (1962).
2. Birks, J. B. and Cameron, A. J. W. *Proc. Roy. Soc.* **249A**, 297 (1959).
3. Tanaka, J., *Bull. Chem. Soc.* (*Japan*) **36**, 1237 (1963).
4. Chu, N. Y. C., Kawaoka, K. and Kearns, D. R., *J. Chem. Phys.* **55**, (1971).
5. Klöpffer, W. and Bauser, H., *Chem. Phys. Letters* **6**, 279 (1970).
6. Birks, J. B. and Kazzaz, A. A., *Proc. Roy. Soc.* **304A**, 291 (1968).
7. Ferguson. J. *J. Chem. Phys.* **28**, 765 (1958).
8. Kim, J. J., Beardslee, R. A., Phillips, D. T. and Offen, H. W. *J. Chem. Phys.* **51**, 2761 (1969).
9. Chandra, A. K. and Lim, E. C., *J. Chem. Phys.* **49**, 5066 (1968).
10. Chandross, E. A. and Dempster, C. J., *J. Am. Chem. Soc.* **92**, 704 (1970).
11. Hochstrasser, R. M., *J. Chem. Phys.* **40**, 2559 (1964).