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

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Version of record first published: 28 Mar 2007.

To cite this article: Robin M. Hochstrasser & Angelos Malliaris (1970): The Luminescence of the Pyrene-Perylene System: Evidence for Mixed Excimers in the Solid State, Molecular Crystals and Liquid Crystals, 11:4, 331-342

To link to this article: http://dx.doi.org/10.1080/15421407008083525

Molecular Crystals and Liquid Crystals. 1970. Vol. 11, pp. 331–342

Printed in Great Britain

The Luminescence of the Pyrene-Perylene System: Evidence for Mixed Excimers in the Solid State†

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Received September 8, 1970

Abstract—Absorption and fluorescence data are presented for the mixed crystal system—perylene in pyrene. It is shown that there is an anomalous luminescence from the mixed crystals above ca. 125 °K, at which temperature we suggest there is a phase transition occurring in the host lattice.

The anomalous emission is studied between 125 °K and 450 °K and the temperature dependence of its spectral shape and location is consistent with there being two superimposed emission spectra, one corresponding to a perylene weakly associated with pyrene, and the other corresponding to perylene more strongly associated to host molecules. The latter emission is spectrally diffuse, and could be the mixed excimer, or exciplex of perylene and host pyrene.

1. Introduction

Sometime ago the fluorescence emission from dilute substitutional solid solutions of pyrene containing perylene was interpreted as being caused by mixed excimers (now called exciplexes) formed by the interaction between an electronically excited perylene molecule and ground state pyrene molecules.[1] A considerable number of reports[2–4] have since appeared on this important prototype system, and much of that work claims to be at variance with the original interpretations and experimental results. The purpose of this paper is to extend and to demonstrate the essential correctness of the original interpretations.

The work we shall present is in agreement with the conclusions

† This work was supported by the Advanced Research Projects Agency Contract SD-69, to the University of Pennsylvania.

in the recent paper by Tomkiewicz and Loewenthal[5] who have shown that electronically excited pyrene-perylene mixtures manifest a bound state involving a perylene and at least one but perhaps two pyrene molecules. However we have some additional results that should lay to rest any doubts about the occurrence of the proposed phenomena.

2. Experimental

Precautions were taken to ensure that the emission spectra were completely free of reabsorption effects. Such effects can produce confusing distortions of the spectrum due to the very high oscillator strength of the first transition of perylene molecule (f = 0.44 in n-heptane solution[6]). Figure 1 shows the absorption and fluorescence of perylene in n-heptane.

The fluorescence from mixed crystals of perylene in pyrene, even for thin samples (ca. 10^{-5} cm) depends on the perylene concentration. In Fig. 2 the emission from samples of different concentrations is shown: In the range between 10^{-4} to 10^{-5} M there was no change in

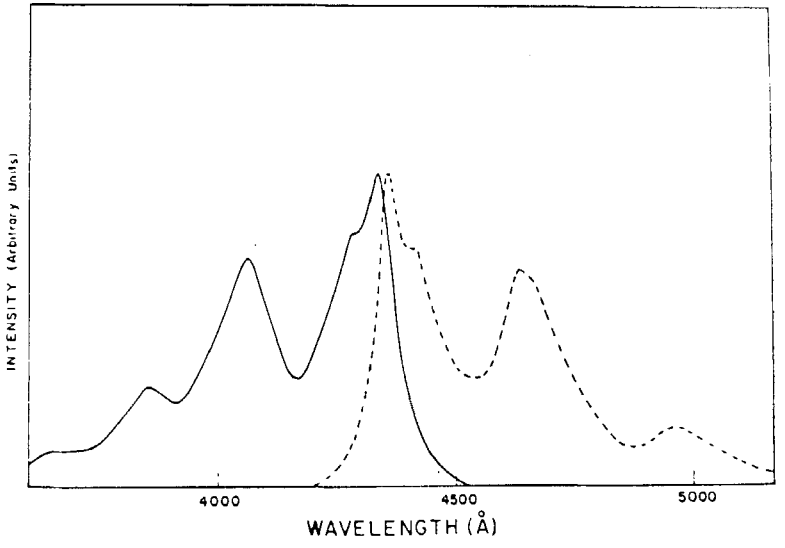

Figure 1. Absorption-fluorescence spectra of a very dilute solution of perylene in n-heptane, at 300 °K.

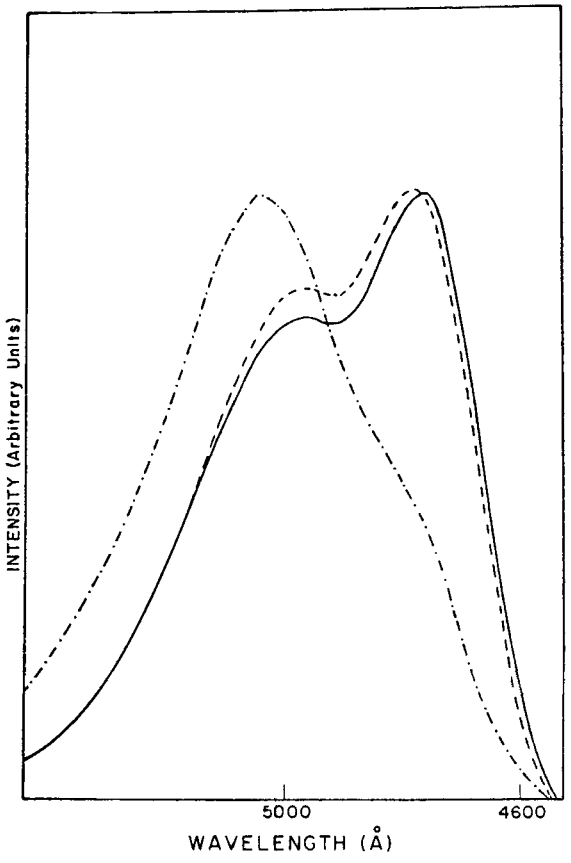

Figure 2. Fluorescence from thin mixed crystals of perylene in pyrene.
— · — · — · 10^{-2} M.
— — — — 10^{-3} M.
———— 10^{-4} M.

the shape of the fluorescence from very thin crystals excited in the perylene bands, and this emission was taken as the actual mixed crystal fluorescence. Crystals with 10^{-6} M perylene showed only pyrene excimer emission when the exciting light was absorbed by the host. In absorption, on the other hand, we did not detect any change with concentration (10^{-3} – 10^{-4} M) in either the spectral location or the relative intensities of the bands. The reported spectra correspond to concentrations of 10^{-3} M for absorption and 10^{-4} M for emission. Three different mercury lines were used (3650, 4060, and 4358 Å)

with essentially the same fluorescence spectrum resulting from each.

Figure 3 shows emission and absorption spectra of thin mixed crystals of perylene in pyrene at room temperature, 77° and 4.2 °K respectively. These spectra should be compared with the absorption and emission spectra of perylene in n-heptane at room temperature

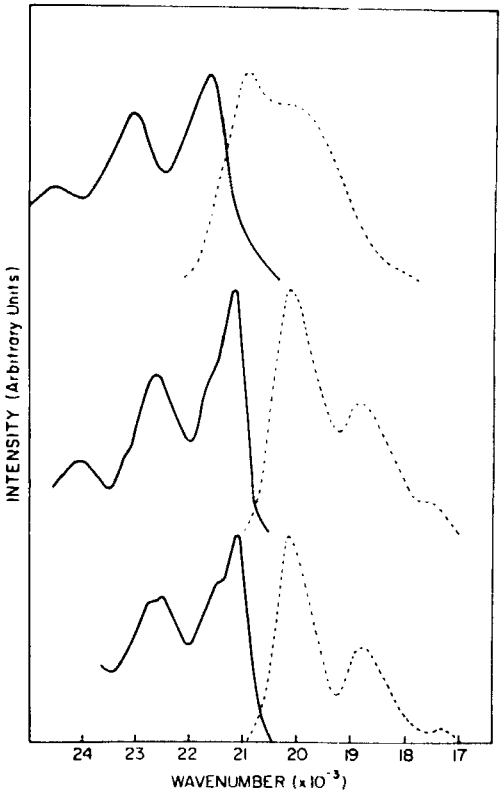

Figure 3. Absorption-fluorescence spectra of perylene in a pyrene crystal.
(a) Upper: 300 °K
(b) Middle: 77 °K
(c) Lower: 4.2 °K

shown in Fig. 1. There is not a usual correspondence between the mixed crystal absorption and fluorescence at 300 °K and although in absorption we can find frequency intervals that match the monomer vibrations, in emission a new apparent frequency (840 cm^{-1}) appears, and this is the only structure observed (cf. Fig. 1).

The vast difference between the room temperature absorption and fluorescence spectrum, most probably evidences an excited state interaction. Since the liquid helium and liquid nitrogen temperature emission and absorption spectra are more similar to the perylene monomer spectrum of Fig. 1, and since the approximate mirror image relationship holds quite well for these low temperature crystal spectra, we can conclude that only at the higher temperatures was the resulting excited state interaction strong enough to alter the fluorescence spectrum. In other words the nuclear displacement necessary for equilibration in the excited state cannot occur in the low temperature crystals.

More vibronic bands show up in absorption as the temperature decreases from 300° down to 4.2 °K, this is of course a normal improvement in resolution due to the lowering of the temperature, and has no particular significance to the process of interest here. The *emission spectra on the other hand do not show much improved resolution at low temperatures.*

By close examination of the emission in the temperature range 300 °K to 77 °K we found that a sudden change in the fluorescence occurs at about 125 °K. Below this temperature we were observing the low temperature spectrum (Figs. 3b. and 3c.) whereas above 125 °K a continuous change of the shape of the spectrum towards the 300 °K emission (Fig. 3a.) was observed. From this temperature discontinuity in the fluorescence we concluded that probably the differences in the spectra at 77° and 300 °K was caused by a sudden change in the crystal structure around 125 °K. In Fig. 4, the emission from a thin sample of the pyrene-perylene mixed crystal is shown, at two temperatures, just above and below the temperature where the sudden change in the fluorescence occurs. Figure 5 shows that the 4770 Å and the 4950 Å peaks of the emission from the mixed crystal, *as well as the 4665 Å peak of the pure crystalline pyrene emission,* undergo a rather abrupt change of their intensity around 125 °K. These measurements were made by observing the fluorescence of a crystal mounted on a chromel-alumel thermocouple. Jacobs and Parks[7] have measured the heat capacity of pyrene crystals from about 20 °K up to 300°, and they found changes to suggest that a phase transition occurs at 116 °K. Our measurements of the phase transition point are not very accurate. In Fig. 5 one can see that

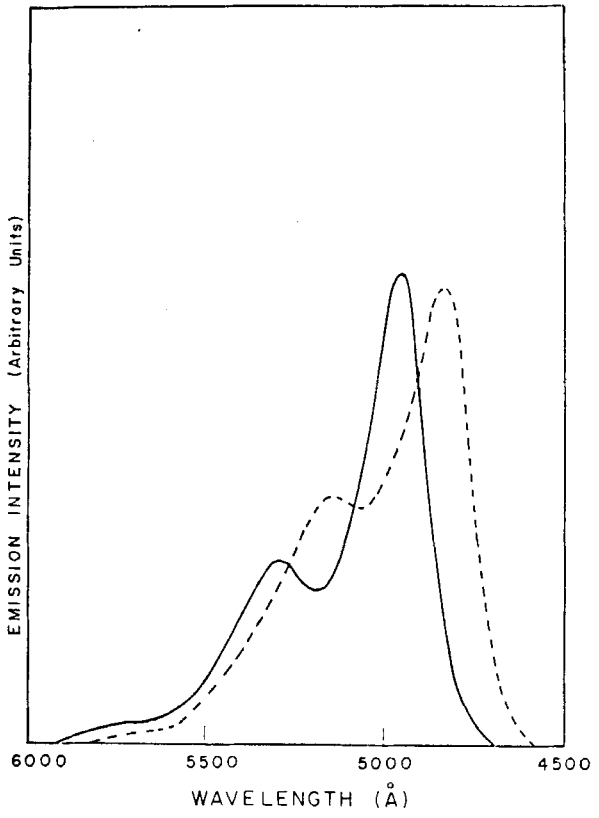

Figure 4. Pyrene-perylene mixed crystal fluorescence; a few degrees above (—), and a few degrees below (— —) the phase transition temperature.

the three curves do not give exactly the same transition temperature but these differences are very likely due to experimental error as well as to detailed points of interpretation.

Additional evidence of the phase transition occurring around 125 °K, is provided by the temperature dependence of the weak resolved emission transitions appearing on the *high energy side* of the otherwise continuous pyrene crystal excimer fluorescence from pure pyrene crystals. These shoulders disappear below about 125 °K and they show up again above this temperature.

We have recorded emission and absorption spectra of the mixed crystal every 10° from 77° up to 450 °K. Although there was, as we

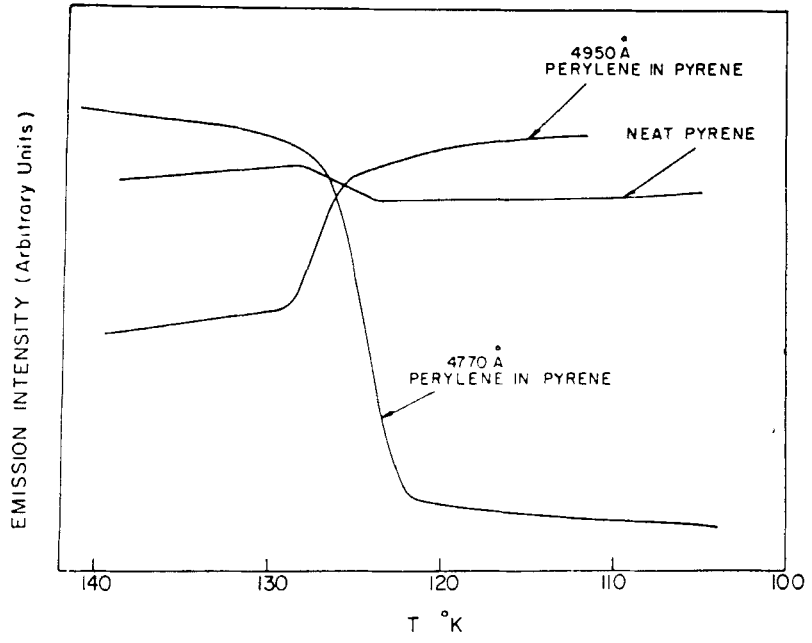

Figure 5. Intensity versus absolute temperature of:
a. 4950 Å band of perylene emission in pyrene crystal
b. 4770 Å band of perylene emission in pyrene crystal
c. Pyrene excimer emission from neat pyrene crystal

mentioned, a sudden change at 125 °K, we noticed a continuous change of the spectrum from 125 °K up to 450°, and concluded that above 125 °K there are two different kinds of emission whose relative intensity is temperature dependent. The spectral shift of the first strong emission peak was, at all temperatures, followed by a similar shift of the corresponding absorption band evidencing the rough mirror image relationship for the perylene emission and absorption from the mixed crystal. In other words apart from the modification of the crystal emission due to the assumed mixed excimer fluorescence (see below) the remnant emission and absorption of the mixed crystal display a fairly constant Stokes shift.

Strictly speaking it will not be correct to call the crystal emission at low temperature monomeric perylene fluorescence, since it is the emission of a weakly associated complex of pyrene and perylene and it is not the emission of isolated perylene molecules: It will be

referred to as pyrene-perylene dimeric emission, although the participation of more than one pyrene is not excluded. When this emission is subtracted from the crystal fluorescence spectrum, as shown in Fig. 6, and after normalizing the two spectra and allowing for the normal broadening of the dimer emission due to the changes

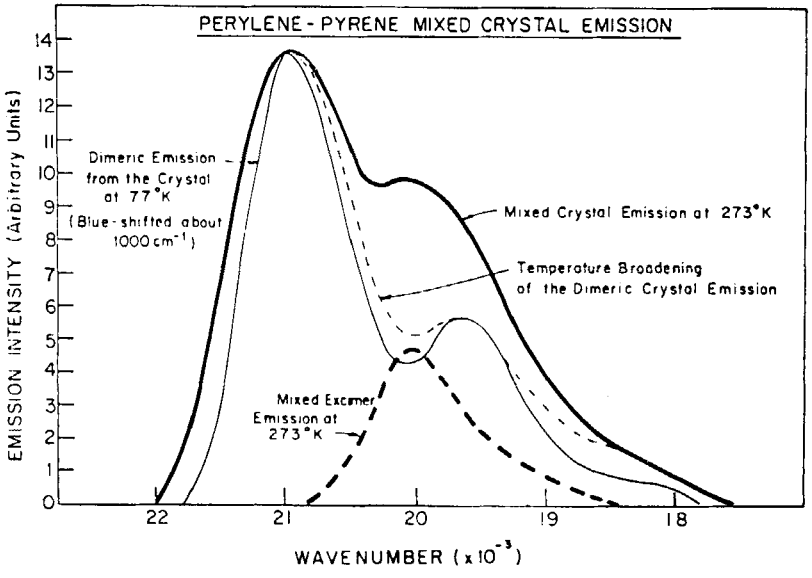

Figure 6. Diagram exposing the possible pyrene-perylene mixed excimer emission spectrum by subtracting the pyrene-perylene dimeric emission from the room temperature emission of the mixed crystal (see text).

in temperature we are left with what resembles a structureless spectrum, which could be emission from the mixed excimer formed from pyrene and one excited perylene molecule.

Figure 7 presents the plot of the logarithm of the ratio of the emission intensities of the pyrene-perylene mixed excimer to the pyrene-perylene dimer, versus the inverse of the absolute temperature at which this ratio was measured. A straight line is obtained whose slope is interpreted as $-E/R$, where E is an Arrhenius energy which is possibly the activation energy for formation of a mixed excimer: It is assumed that the fraction of molecules forming mixed excimers is proportional to the relative intensity of the mixed excimer emission. The activation energy so measured is 65.8 cm^{-1}.

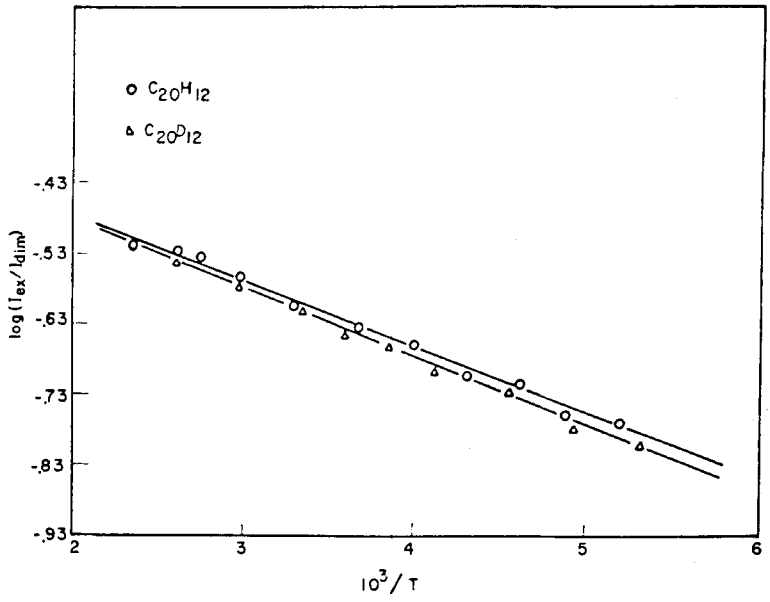

Figure 7. Plot of the logarithm of the intensity ratio of the assumed pyrene-perylene excimer, versus the inverse of the absolute temperature.

Mixed crystals of perylene – d_{12} in pyrene (h_{10}) gave essentially the same fluorescence apart from a 100 cm^{-1} blue shift of the emission peak that we attribute to the mixed excimer. The blue shift with respect to the mixed excimer formed from the protomolecules, is due to the higher energy of deuterated perylene's lowest excited singlet state.

The fact that the assumed mixed excimer fluorescence is continuously blue-shifted as the temperature is increased (from 125 up to 300 °K) has been observed with neat crystal excimers such as pyrene,[8] perylene,[9] ovalene.[10] This shift is possibly due to a continuous reorientation of the molecules in the lattice with changing temperature.

3. Energy Estimates

Several calculations of the excimer energy have been made during recent years: Here we are interested in whether a mixed excimer

of the conjectured type can have a transition energy that can be roughly predicted by simple calculations.

There are a number of approaches available for calculating the excimer energy. One is based on the exciton theory and employs configurational mixing between a neutral exciton state and a charge-transfer state.[2,11,13] Another method views the two molecules as a supermolecule and the energies are calculated by the LCAO-MO approximation.[14]

To obtain an estimate we have used the first method but without explicitly working out the configurational interaction between the charge transfer and the exciton states. Instead we have used the values for $\langle CT \mid 1/r \mid Ex \rangle$ matrix elements previously calculated[2] for the perylene dimer. The assumption that those matrix elements are similar for the perylene dimer and for our pyrene-perylene mixed dimer is quite reasonable, especially since the charge-transfer exciton interaction is very similar for the case of dimers of naphthalene, anthracene, pyrene and perylene. By expressing the interaction $\langle CT \mid 1/r \mid Ex \rangle = V$ as a function of the type $V(R) = Ae^{-BR}$ we find that $V(R) = 211e^{-1.89R}$eV. From this equation we have calculated V(R) for various values of R(Å) the intermolecular separation.

The computation of the neutral exciton states followed known methods,[13] but we used second-order perturbation theory since the zero-order states are separated by 7000 cm^{-1}. (This is the separation between the first singlet excited state of perylene and the second singlet excited state of pyrene). The energies of the zero-order CT states were found by calculating the Coulomb interactions and using experimental values of ionization potentials, and theoretical values for electron affinities. Some of the numerical results are given in Table 1, and the results are summarized in Fig. 8. In Fig. 8—which is drawn to scale—we have *estimated* the ground state destabilization. This calculation is simply meant to demonstrate the reasonableness of the mixed-excimer stabilization. The lowest state of the system is *mainly* a perylene state, but the strong dependence of the total energy on the intermolecular separation makes such a state easily distinguishable, by optical spectroscopy, from that of a normal isolated molecule.

A further refinement can be made by including more than one pyrene molecule into the 'exciplex' since this is indeed a mixed

TABLE 1 Calculated Values for the Charge-transfer (CT), Lowest-exciton (E) and Mixed Excimer Level (E_{mix}) of the Pyrene-Perylene Dimer.

R(Å)	(a) C(eV)	CT(eV)	E(eV)	(b) E_{corr}(eV)	E_{mix}(eV)
3.0	3.03	3.12	2.747	2.834	2.25
3.5	2.77	3.38	2.793	2.846	2.72
4.0	2.54	3.61	2.820	2.851	2.846

(a) C is the Coulomb attraction between the two ions, Py^- and Pe^+

(b) This is the calculated value for the lowest exciton state corrected by using the scaling factor $(M_{obs}/M_{cal})^2$.

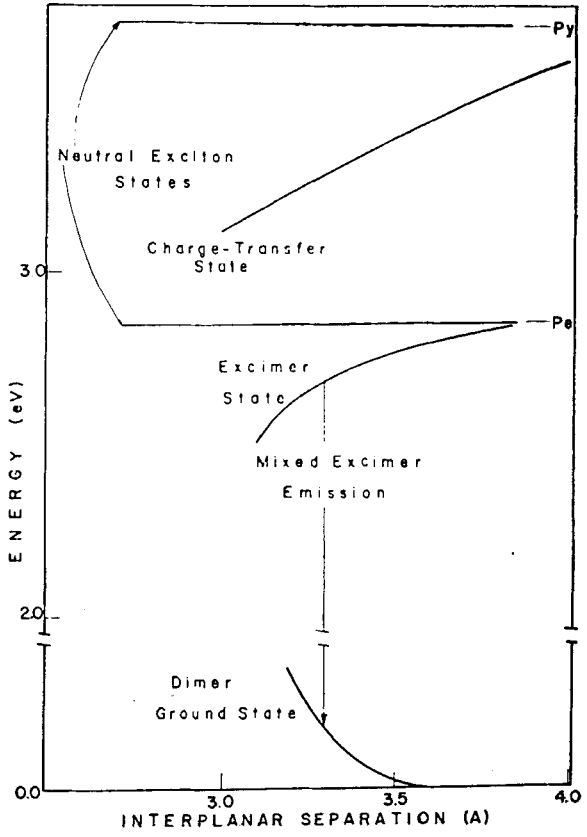

Figure 8. Energy vs intermolecular separation of the neutral exciton, the charge-transfer and the mixed excimer states.

crystal phenomenon. This suggestion was already made by Tomkiewicz and Loewenthal,[5] and we agree that in a pyrene polymer—excited perylene complex the interactions could be more favorable for exciplex formation since I + A for perylene is more different from I + A of a pyrene polymer than of a single pyrene molecule. In any event we wish to emphasize that the perylene molecule is interacting with pyrene *in a pyrene crystal* wherein the pyrene states are not the same as those for isolated molecules, nor are the parameters such as the effective I and A the same in the crystal. Since I + A for isolated pyrene is probably about the same as for isolated perylene it is not so surprising that we have failed to observe this mixed excimer in solutions.[10,15] The solid-state effects described here should be quite common in mixed crystals with components having very different I + A.

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15. We have gone to some lengths using extremely concentrated solutions in extremely polar solvents and in other systems but we have not detected an emission that we could ascribe with certainty to the mixed excimer.