On the Use of Perhydrocoronene as a Matrix in the Luminescence Spectroscopy of Polycyclic Aromatic Hydrocarbons

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Higher molecular polycyclic aromatic hydrocarbons (PAH) form supersaturated solid solutions in perhydrocoronene. With coronene as the solute, concentration-dependent P-type delayed fluorescence is observed at 77 K. Even very small amounts of coronene, present as an impurity in the perhydrocoronene matrix, can lead to quenching of the phosphorescence of an added guest PAH by intermolecular triplet-triplet energy transfer and to sensitized coronene phosphorescence when the lowest triplet state of the added guest molecule lies higher in energy than that of coronene. Thermal band broadening of guest molecule phosphorescence has been studied in the temperature range from 77 to 433 K.

We have previously reported on fluorescence and phosphorescence properties of coronene (**1**) and hexabenzo[bc,ef,hi,kl,no,qr]coronene (**2**) studied in perhydrocoronene (PHC) ($C_{24}H_{36}$) as a matrix [1]. In the present communication we deal with some general features of the use of PHC as a matrix in the luminescence spectroscopy of polycyclic aromatic hydrocarbons (PAH). The following subjects will be discussed: (i) Molecular structure of the solid PAH/PHC systems; (ii) role of intermolecular triplet-triplet energy transfer in PAH/PHC systems; (iii) temperature dependence of PAH phosphorescence spectra in PHC.

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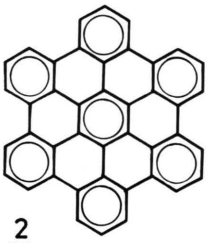

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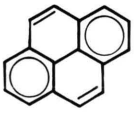

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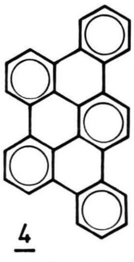

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1. Results and Discussion

1.1. On the Molecular Structure of the Solid PAH/PHC Systems

Many PAHs exhibit vibronically well-resolved fluorescence/phosphorescence spectra in PHC at 77 K. Two examples (hydrocarbons **1** and **2**) have been given in our previous paper [1]. A further example is shown in Figure 1. Curve a is the fluorescence spectrum of

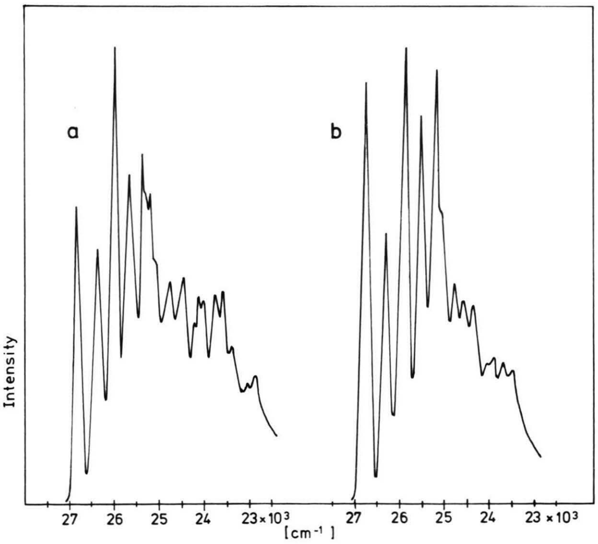

Fig. 1. Fluorescence spectra of pyrene (**3**) at 77 K in perhydrocoronene (pyrene concentration: 1%) (curve a) and in a n-hexane/cyclohexane mixture (9:1, vol/vol; pyrene concentration: 10^{-4} M) (curve b). (The spectra have been normalized to the intensity of the most intense band.)

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pyrene (**3**) (1%) in PHC at 77 K while curve b is the fluorescence spectrum of **3** (10^{-4} M) in a n-hexane/cyclohexane mixture (9:1, vol/vol) measured under otherwise identical conditions.

It is very likely that the well-resolved fluorescence/phosphorescence spectra of PAH in PHC stem from molecularly dispersed solid solutions. However, some of the PAHs that give fluorescence/phosphorescence spectra in PHC are only very sparingly soluble in organic solvents, particularly in aliphatic hydrocarbons. Therefore it is assumed that in these cases the PAH/PHC mixture forms highly *supersaturated* solutions on melting (m.p. of PHC ≈350 °C) that stay supersaturated on rapid cooling.

In the course of the present work we have observed that solid **1**/PHC solutions also show P-type delayed fluorescence [2] in addition to phosphorescence and E-type delayed fluorescence [1]. The P-type character of the delayed fluorescence has been concluded from the observations that (i) the fluorescence occurs at low temperature (77 K) and (ii) has a shorter lifetime than the simultaneously occurring phosphorescence. Figure 2 shows the total delayed luminescence spectrum as well as the luminescence decay curves of a sample obtained by melting a mixture of 10% **1** and 90% PHC following rapid cooling to 77 K. In Fig. 3 the ratio ($I_{\text{P-DF}}/I_{\text{P}}$) of the intensity of the P-type delayed fluorescence ($I_{\text{P-DF}}$) and phosphorescence (I_{P}) is plotted against coronene concentration (weight-%). With increasing coronene concentration the ratio ($I_{\text{P-DF}}/I_{\text{P}}$) also increases.

It is well established that triplet-triplet ($^3M^* - {}^3M^*$) annihilation yielding P-type delayed $^1M^*$ fluorescence can occur in both rigid solutions [3] and pure crystals [4]. In the present case it is reasonable to assume that at low concentrations of **1** it forms predominantly molecularly dispersed solid solutions in PHC while at higher concentrations microcrystals (aggregates) of **1** are also present. As organic compounds with long triplet lifetimes do not show phosphorescence in the crystalline state, it has to be concluded that even at relatively high concentrations of **1** a distinct fraction is still present as isolated molecules.

1.2. Intermolecular Triplet-Triplet Energy Transfer in PAH/PHC Systems

The PHC presently available and used in our experiments contains a small amount of coronene (**1**) (shown by phosphorescence) which, however, is less

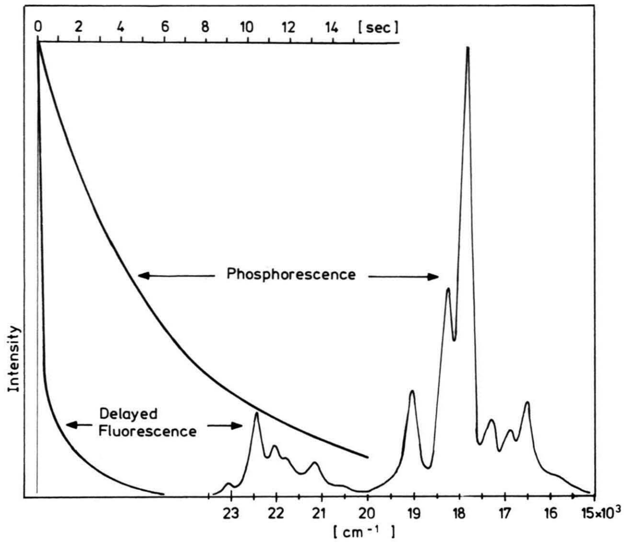

Fig. 2. Total delayed luminescence spectrum and luminescence decay curves of coronene (**1**) (10%) in perhydrocoronene at 77 K.

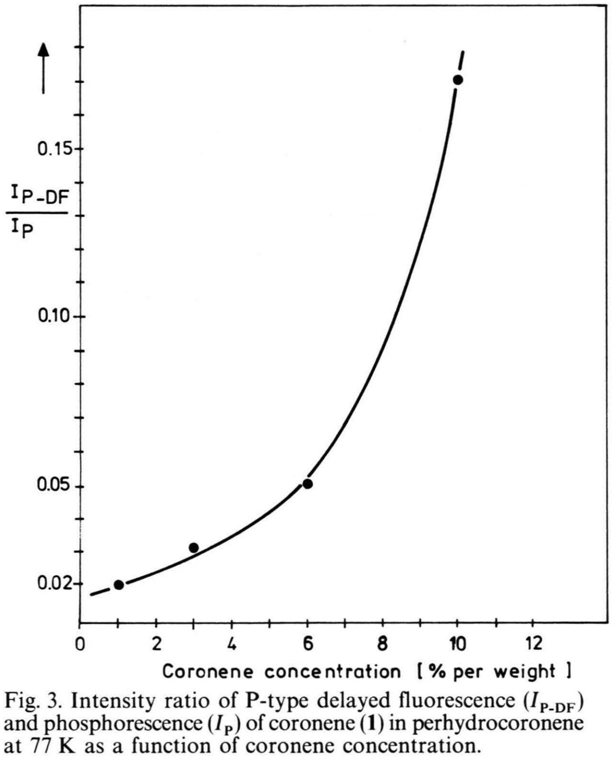

Fig. 3. Intensity ratio of P-type delayed fluorescence ($I_{\text{P-DF}}$) and phosphorescence (I_{P}) of coronene (**1**) in perhydrocoronene at 77 K as a function of coronene concentration.

than $3 \cdot 10^{-4}\%$ (determined by UV absorption) [1]. This very mall amount of **1** leads to phosphorescence quenching by intermolecular triplet-triplet energy transfer when PAHs are examined in PHC whose lowest triplet (T_1) state energy lies above 19 210 cm^{-1}, i.e. above the T_1 state energy of coronene. In these cases the observed phosphorescence is dominated by the sensitized phosphorescence of **1** while the characteristic phosphorescence bands of the PAH to be studied appear with low intensity. This effect is not observed with PAHs having their T_1 state below that of coronene.

As we have to use in most cases rather high concentrations (0.1 – 1%) of guest PAH, the distances between PAH guest molecules and coronene molecules are small; as a result, intermolecular triplet-triplet energy transfer is very efficient. Furthermore, the phosphorescence quantum efficiency of coronene is higher than that of most guest PAHs studied. Excitation of coronene phosphorescence by intermolecular triplet-triplet energy transfer has been found to be much more efficient than direct optical excitation. This again is due to the relatively high PAH guest molecule concentrations used.

The effect, of course, is not inevitable but depends simply on the purity of the PHC used.

1.3. On the Temperature Dependence of PAH Phosphorescence Spectra in PHC

In our previous paper [1] we have mentioned that PHC can be used as a matrix in luminescence spectroscopy of PAHs up to fairly high temperatures. In the course of the present work we have examined the temperature dependence of phosphorescence bandwidths of PAHs dissolved in PHC. As an example, the half-width of the first phosphorescence band (at 18 553 cm^{-1}) of tribenzo[fg,ij,rst]pentaphene (**4**), determined in the temperature range from 77 to 433 K, is given in Table 1.

Table 1. Band half width of the first phosphorescence band of tribenzo[fg,ij,rst]pentaphene (**4**) as a function of temperature.

Temperature [K]	Band half-width [cm^{-1}]	Temperature [K]	Band half-width [cm^{-1}]
77	343	293	543
103	343	333	679
143	343	353	800
193	378	373	927
233	444	433	1139

2. Experimental

All experiments were performed as described in [1] and references cited therein. A Perkin-Elmer MPF 44 E spectrofluorimeter was used for the fluorescence measurements of pyrene.

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