Triplet State Properties of Binary Mixed Crystals of Dibenzofuran and Fluorene

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Phosphorescence spectra and ODMR measurements at 1.3 K on a series of 13 mixed crystals of dibenzofuran (DBF) and fluorene (F) as well as of neat crystals of DBF and F (X-traps) are reported. Drastic changes in the spectra with different F:DBF ratios are observed, demonstrating the possibility of investigations of the electronic properties of F monomers, dimers, trimers and larger aggregates in this mixed crystal system of two chemically different molecules.

I. Introduction

Concentrations of 1% or more of substitutionally incorporated guest molecules in molecular crystals are not very common, except for isotopically mixed crystals like naphthalene-h_8 in naphthalene-d_8 [1]. Such isotopic mixed systems do not deviate much from a periodic one and can therefore be treated by perturbation techniques [2] for the understanding of their spectra.

Some chemically different organic molecules with very similar molecular and crystal structure data form solid solutions. They allow one to grow single crystals from the melt at any suitable concentration. Electronic spectra of such substitutionally incorporated guest molecules can be useful for understanding energy transfer in mixed crystals and even in disordered systems. They give further information about the electronic states of isolated guest molecules at low concentration, of dimeric, trimeric and more highly aggregated states at higher concentrations and guest exciton bands at even higher concentrations of about 30% or more. Recently Vaida and Colson [3] reported results on triplet energy migration in p-dichlorobenzene-p-dibromobenzene solid solutions.

Here, we report the first results on optical investigations of the triplet state properties of another binary mixed crystal system: dibenzofuran (DBF) and fluorene (F) (Figure 1). They can be mixed in any proportions and form well defined molecular crystals with developed cleavage planes. Both molecules are very similar in shape and size
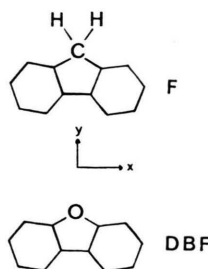

Fig. 1. Molecules: top fluorene (F), bottom dibenzofuran (DBF).

and form orthorhombic (D_{2h}) crystals [4, 5], with four molecules per unit cell. All four molecules have their x-axes parallel to the c-axis of the crystals, while the y-axes of DBF and F form angles of 27.5° and 34.8° with the b-axis. The property of forming solid solutions was already pointed out by Lüttringhaus and Hauschild in 1940 [6] and was appearant from the melting point and solidification data at various concentrations.

An important aspect of the optical studies on this mixed crystal system is the use of synthesized DBF and F [7] in order to obtain the material free from impurities (< 50 ppm) after zone refining.

At 1.3 K neat crystals of DBF and F show fluorescence [8] and phosphorescence [7] of shallow X-traps due to crystal imperfections. The first excited singlet state S_1 of DBF X-traps lies 299 cm^{-1} below the S_1-state of F X-traps ($S_1 = 32834$ cm^{-1}, [8]), while the triplet state T_1 of F X-traps lies 939 cm^{-1} energetically lower than the one of DBF X-traps ($T_1 = 24546$ cm^{-1}, [7]) in the neat crystals, showing that for the triplet system F forms a deep trap with respect to the DBF triplet exciton band.

The electronic properties of the triplet states of DBF and F X-traps in neat crystals were investigated by us recently [7].

We present here phosphorescence spectra at 1.3 K for a series of mixed crystals of different concentrations of F in DBF. Optical detection of magnetic resonance (ODMR) in zero field was used in order to clarify the interpretation of these spectra.

II. Experimental

Synthesized DBF and F with a total impurity concentration below 50 ppm was used for the preparation of the crystals [7]. The synthesis of these hydrocarbons and the determination of the impurity concentrations after zone refining is described in [7]. Crystals were grown from the melt by the Bridgman-method.

Phosphorescence spectra were taken from neat crystals of DBF and F (X-traps) as well as of 13 mixed crystals of different concentrations of F and DBF (see Figure 2). For the measurements of the phosphorescence spectra the samples were placed in a liquid Helium Dewar and the temperature reduced to 1.3 K by pumping. The crystals were excited at a wave-length of 300 nm using a 250 W mercury lamp, and a 1/4 m Schoeffel monochromator. Additional filters UG 5, UG 11 and broadband Schott UV/R-280, UV/R-310 interference filter were used. The phosphorescence was monitored at right angles to the excitation path with a 0.85 m Spex grating monochromator (1402) using narrow slits (between 10/10 μ and 200/200 μ ≙ 0.01−0.2 nm bandpath) [7].

The spectra shown in Fig. 2 were observed without using a rotor system to make sure that the emissions are not masked in their early time history. Nevertheless, it was proved with a rotor system that all the emissions shown in Fig. 2 originate from triplet states.

The ODMR-apparatus was essentially the same as described by Zuclich et al. [9].

III. Results

Figure 2 shows the phosphorescence spectra of neat DBF (X-traps, 0, 0-line 407.4 nm ≙ 24546 cm^{-1}, 2a), and neat F crystals (X-traps, 0, 0-line

423.6 nm ≙ 23607 cm^{-1}, 2p) as well as of 13 mixed crystals with increasing concentrations of F in DBF (2b−2o).
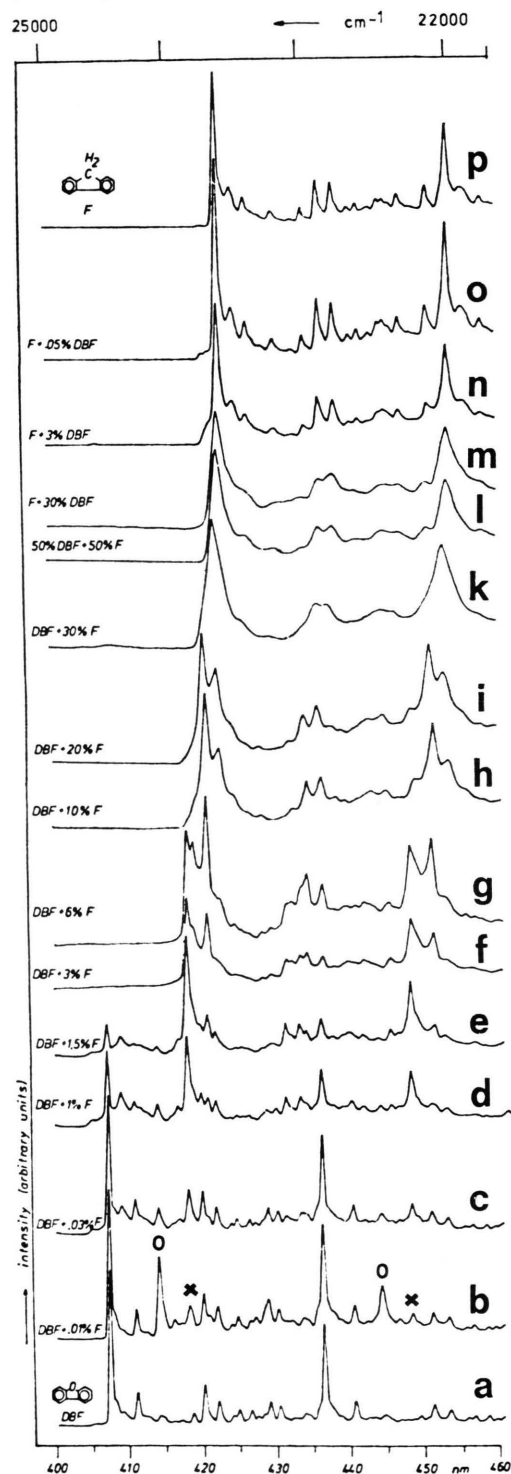

Fig. 2. Phosphorescence spectra at 1.3 K of neat DBF (X-traps) 2a and neat F (X-traps) 2p crystals as well as of 13 mixed crystals of different concentrations of F and DBF: 2b 0.01% F, 2c 0.03% F, 2d 1% F, 2e 1.5% F, 2f 3% F, 2g 6% F, 2h 10% F, 2i 20% F, 2k 30% F, 2l 50% F, 2m 70% F, 2n 97% F, and 2o 99.95% F.

Table 1. Triplet zero field splitting parameters $|D|$ and $|E|$ of dibenzofuran (DBF) X-traps and fluorene (F) X-traps in neat crystals as well as of F-monomers in DBF (detected at 418.5 nm $\triangleq 23895$ cm^{-1} at a concentration of 0.01% F in DBF) and of large F-clusters at a concentration of 30% F in DBF (detected in the range between $421.0 - 425.0$ nm $\triangleq 23753 - 23529$ cm^{-1}) as detected by ODMR in zero field at 1.3 K. For comparison the $|D|$ and $|E|$ value of DBF and F at low concentration in n-heptan is [7]: $|D| = 0.1085$ cm^{-1}, $|E| = 0.0093$ cm^{-1} for DBF and $|D| = 0.1094$ cm^{-1}, $|E| = 0.036$ cm^{-1} for F.

	crystals	$|D|$ [cm^{-1}]	$|E|$ [cm^{-1}]
Dibenzo-furan (DBF)	X-traps in neat crystals	0.1073	0.0099
Fluorene (F)	monomer in 0.01% F in DBF	0.1089	0.041
	large clusters in 30% F in DBF	0.1071	0.038
	X-traps in neat F crystals	0.1061	0.030

The phosphorescence spectra of the X-traps of neat DBF (2a) and F crystals (2p) show very similar vibronic structures. The spectrum of the neat F crystal is virtually identical to the spectra shown by Bree and Zwarich [10]. The linewidth of the vibronic phosphorescence bands of both spectra (2a and p) is about $2\,\text{Å} \triangleq 12$ cm^{-1}. This relatively large linewidth without any indication of phonon structure indicates large inhomogeneous broadening, suggesting a large variety of crystal imperfections [7].

Table 1 shows the triplet zero field splitting parameters $|D|$ and $|E|$ as measured by ODMR in zero field at 1.3 K of DBF X-traps in the neat crystal, F molecules in a mixed crystal of DBF and F with a F concentration of 0.01%, of F clusters at a concentration of 30% F in DBF and of F X-traps in

Fig. 3. Dependence of the $2|E|$ transition of fluorene on the detection wavelength for a mixed crystal of DBF $+ 6\%$ F (x) as well as for a DBF$+ 30\%$ F (o) crystal (1.3 K, monochromator bandwidth 0.2 nm).

the neat crystal. In addition Fig. 3 shows the dependence of the $2\,|E|$-transition of F on the detection wavelength for a DBF $+ 6\%$ F crystal as well as for a DBF $+ 30\%$ F crystal. These measurements were made with a 0.2 nm monochromator bandwidth.

IV. Discussion

The discussion of the phosphorescence spectra will be divided into 3 parts covering the F concentration in the ranges up to 1.5%, up to 20% and larger than 20%.

Beside the F trap emission the mixed crystals with F concentrations up to 1.5% (Fig. 2b—e) still show phosphorescence of DBF X-traps as can be seen by comparison with the spectrum of the neat DBF crystal (Figure 2a). The DBF X-traps are characterized by the triplet zero field splitting parameters D and E shown in Table 1.

In the mixed crystal with the lowest guest concentration of F (0.01%) studied by us, the F monomer phosphorescence (Fig. 2b, ($\times$)) appears at 418.5 nm $\triangleq 23895$ cm^{-1} with a progression of 1604 cm^{-1} (1605 cm^{-1} for F X-traps in the neat F crystal) with relatively low intensity and lies 651 cm^{-1} below the 0, 0-line of the DBF X-trap phosphorescence, but 288 cm^{-1} above the 0, 0 line of the F X-trap phosphorescence in the neat F crystal (Figure 2p). The F monomers in Fig. 2b, ($\times$) were identified by the triplet zero field splitting parameters D and E and by comparison with those of F in low concentration in a polycrystalline n-heptane matrix (see Table 1).

In the mixed crystal with 0.01% F further two relatively intense lines (Fig. 2b, (o)) appear at 414.2 nm $\triangleq 24143$ cm^{-1} and 444.3 nm $\triangleq 22507$ cm^{-1}. The line at 414.2 nm lies energetically between the 0, 0 emissions of the DBF X-traps and of the F monomers.

The origin of these two lines is unclear. The two ODMR zero field transitions of 444.9 MHz and 2.975 GHz observed on these lines do neither belong to DBF X-traps nor to F monomers, F clusters or F X-traps. Because of the low F concentration and since this emission could not be observed in the neat DBF crystal (proved by ODMR) these phosphorescence lines cannot have their origin in a small impurity concentration. Further these unindentified two phosphorescence
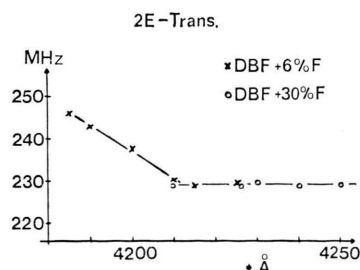
lines could also be observed in the mixed crystals with 0.03% F, 1% F and 1.5% F (proved by ODMR), but the intensities of these two lines decrease with the increasing F concentration. We assume that the phosphorescence might result from a heteroexcimer formed by F and DBF molecules. On the other hand, the fact that these lines (Fig. 2b, (○)) show a progression of 1636 cm^{-1} may indicate that this emission might come from a DBF pair state (1637 cm^{-1} for DBF X-traps in the neat DBF crystal), induced by F molecules.

With increasing F concentration it is also observed that the intensity of the DBF X-trap emission decreases. At a concentration of 1% F in DBF the intensity of the 0, 0 line (24546 cm^{-1}) of the DBF X-traps is about the same as the intensity of the 0, 0 line of the lower lying F monomer emission (23895 cm^{-1}). This demonstrates negligible depopulation of the DBF X-traps via the exciton band into the F monomer traps at F concentrations lower than 1%.

At higher F concentrations energy transfer can be enhanced by F chains or clusters which extend throughout the crystal. At a concentration of 1.5% F in DBF (Fig. 2e) the 0, 0 line of the F monomers appears as the strongest phosphorescence line in the spectrum. At a concentration of 3% F all phosphorescence comes from the F molecules (Fig. 3f) and the DBF X-traps cannot be observed anymore by ODMR.

The phosphorescence spectra of the mixed crystals in the concentration range between 3% and 20% F in DBF is characterized by emissions of F monomers, dimers, trimers and aggregates. This can be seen from the additional phosphorescence lines appearing in the range between 418.5 nm and 425.0 nm ≙ 23895 cm^{-1} and 23529 cm^{-1} for instance in the spectrum of the mixed crystal of 6% F in DBF (Figure 2g). The zero field splitting parameters D and E of the F monomers, dimers, trimers and higher aggregates vary slightly in this wavelength region. Figure 3 shows the wavelength dependence of $2 |E|$ for F at a concentration of 6% in DBF. A monotonically decreasing value of $2 |E|$ for F dimers, trimers etc. is observed in the region between 418.5 nm and 421.0 nm while in the region of larger F aggregates between 421.0 nm and 422.5 nm the value for this parameter is constant. A very similar behaviour is observed for the D-E transition.

The explanation for the shift of the values of the zero field splitting parameters is that in the case of dimers, trimers and higher aggregates of translationally equivalent F neighbours D and E are slightly smaller than for the isolated F monomer in the DBF matrix. The decrease of the triplet zero field splitting parameters depends on the strength of the π-orbital interaction and the resonance interaction of the translationally equivalent F neighbours and is due to a small contribution of a symmetric charge transfer term to the total wave function as was shown for [2.2]-phanes including two [2.2]-fluorenophanes [11].

There exist in this type of mixed crystals further dimers of translationally inequivalent F neighbours with quite different zero field splitting parameters from the F monomer — similar to the AB pair in the isotopically mixed naphthalene crystals [12]. We tried to observe these by ODMR in zero field, especially in the case of the crystal of 6% F in DBF. We have not yet been able to detect such translationally inequivalent F dimers, but in zero field the conditions for detecting these microwave transitions might not be easy to find, as was shown for the "mini-exciton" (AB pair) in isotopically mixed naphthalene-crystals [13].

At a concentration of 10% F in DBF (Fig. 2h) the F monomer phosphorescence has nearly totally disappeared because of a relatively fast energy transfer from the monomers to F dimers, trimers and other small clusters. As the F concentration increases the phosphorescence lines broaden and the position of the most intense line shifts to lower energies.

At a concentration of 30% F in DBF (Fig. 2k) only one broad emitting F band with the maximum at 422.7 nm ≙ 23657 cm^{-1} is observed. Figure 3 shows the wave-length dependence of the $2 |E|$ transition. Over the whole range from 421−452 nm ≙ 23752−23529 cm^{-1} a constant value of $2 |E|$ is found. The same behaviour is observed for the D-E transition. At this concentration of about 30% F in DBF the static percolation concentration [2], which is defined as the lowest guest concentration at which an infinitely extended guest state is likely to be formed, seems to be reached. This percolation concentration of 30% would agree quite well with a calculated value of 30.7% for a single cubic lattice [2], based on the assumption that only nearest neighbour interactions are important.

In the concentration range of 30—70% in DBF (Fig. 2k—m) the phosphorescence emission bands are still broad but the maximum shifts to lower energy with increasing F concentration.

At concentrations of 97% F and 99.95% F in the mixed crystals (Fig. 2n—o) the F system has to be seen as the host matrix. In these systems the energetically higher lying DBF molecules induce X-traps in the F crystal. The 0, 0 phosphorescence line is narrower than in the mixed crystals with 30%—70% F in DBF. The maximum appears at the same wavelength as the X-traps in the neat F crystal (423.6 nm $\triangleq 23607$ cm^{-1}). The triplet zero field splitting parameters D and E (Table 1) are the same. Nevertheless, investigations with ENDOR [14] on X-traps in F crystals doped with dibenzothiophen and ESR [15] studies on X-traps in neat F crystals have demonstrated the different nature of impurity induced X-traps in F with respect to X-traps in neat F-crystals which are probably due to lattice imperfections. It was shown [15] that in contrast to the impurity induced X-traps in F the CH$_2$ protons in X-traps of neat F crystals have equal bonding angle and are equivalent.

From all the phosphorescence spectra in Fig. 2 drastic changes in the spectra with different F : DBF ratios are observed. The first results reported here demonstrate the possibility of investigations of the electronic states of dimers, trimers and larger aggregates in this new mixed crystal system of two chemically different molecules.

The study of the temperature dependence of the spectra will give further information on the energy transfer in this system. First measurements at higher temperatures (30% F + DBF) have further shown a heteroexcimer emission from a temperature activated complex between F and DBF.

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