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EXCITED STATES OF ACRIDINE - ANTHRACENE MIXED CRYSTALS

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Abstract Single crystals of acridine mixed with anthracene were studied by optical methods in order to establish the structure of low-energy electronic excited states. It was found that anthracene molecules form both singlet and triplet traps for excitons. Singlet excimers of acridine have been observed, but no experimental evidence of triplet acridine excimers has been found.

INTRODUCTION

Acridine - anthracene mixed crystals retain crystal structure of acridine II, where molecules are arranged in two types of parallel pairs, the intermolecular distances in pairs are 3.5 and 3.7 Å respectively¹. The studies of pure acridine II crystal have lead to the concept of singlet excimers formation in such a crystal structure². The formation of triplet excimers has also been postulated despite the lack of the phosphorescence of acridine.

The aim of this work was to investigate single mixed crystals of acridine and anthracene with regard to their electronic structure (both singlet and triplet states) and to verify the concept of singlet and triplet excimers. This work is also a continuation and natural extension of our previous interest of anthracene - acridine mixed crystal (with anthracene being the host)³.

RESULTS AND DISCUSSION

The mixed crystals of acridine with 0.02, 0.1 and 1% mol of anthracene grown by sublimation have been investigated in the temperature range

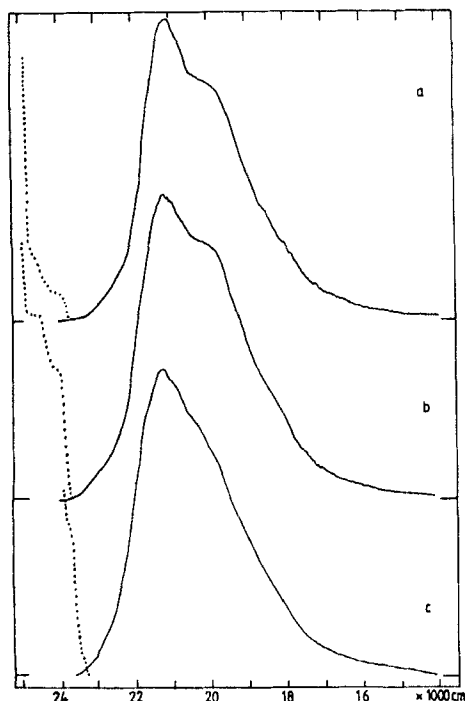


FIGURE 1 The edge of absorption spectra (.....) and fluorescence spectra (—) under excitation at 27470 cm^{-1} and $T=1.7\text{ K}$ of mixed crystals with (a) 0.02, (b) 0.1 and (c) 1 %mol of anthracene.

1.7–300 K.

The fluorescence spectra of mixed crystals (under excitation at 27470 cm^{-1}) recorded at 1.7 K are presented in Fig.1 together with the edge of absorption spectra. Fluorescence spectra of mixed crystals are similar to the fluorescence spectrum of pure acridine II crystal reported in ref.2 and have the same decay time $\tau = 84\text{ ns}$ at 4.2 K. Maxima of these broad spectra are shifted by $\sim 4200\text{ cm}^{-1}$ from the 0-0 transition of acridine absorption spectrum⁴. This is characteristic for excimeric emission so one can conclude that the excitation of mixed crystals to acridine S_1 excitonic band or above the band leads to the formation of acridine excimers.

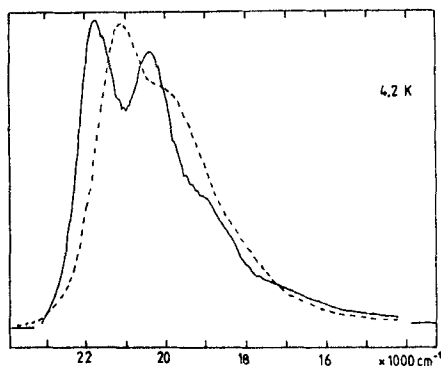


FIGURE 2 The fluorescence spectra of acridine +0.02 %mol anthracene mixed crystal under excitation at 27470 cm^{-1} (---) and 24100 cm^{-1} (—) recorded at $T=4.2\text{ K}$.

Contrary to the absorption spectrum of pure acridine II crystal, the absorption spectra of mixed crystals have the bands lying below the 0-0 transition of acridine absorption. The intensity of bands increases with the concentration of anthracene in a mixed crystal (Fig.1). The excitation tuned to these bands (i.e. 24100 cm^{-1} excitation) leads to the emission of structured fluorescence (Fig.2) decaying at 4.2 K with the decay time of 8ns. This confirms that low-energy states (singlet traps) in a mixed crystal are formed at anthracene molecules. Short decay time and structured fluorescence is characteristic for monomer emission, the possibility of anthracene - acridine exciplex can be ruled out.

Spectra of delayed fluorescence of mixed crystals (Fig.3) excited to or above S_1 excitonic band are broad, and are emitted in the same spectral range as the spectra of prompt fluorescence. At low-energy side of delayed fluorescence the structured spectrum of phosphorescence occurs.

Detailed investigation of phosphorescence shows that it consists of two overlapping spectra: one with the 0-0 transition at 15691 cm^{-1} and decay time 34 ms (at 1.7K), the second with the 0-0 transition at

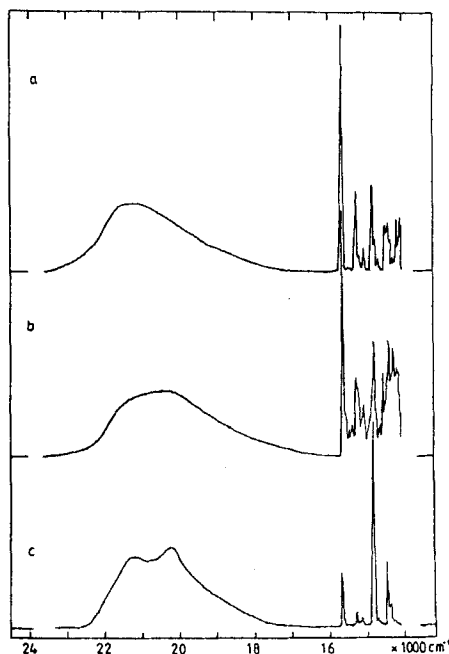


FIGURE 3 Delayed emission spectra of mixed crystals recorded at $T=1.7$ K. Excitation at 27470 cm^{-1} , concentration of anthracene: (a) 0.02, (b) 0.1 and (c) - 1.0 %mol.

14829 cm^{-1} and decay time at 1.7 K $\tau = 40$ ms. The high-energy spectrum dominates in crystals with 0.02 and 0.1 % mol of anthracene (in Fig.3a and 3b its 0-0 is the most intense one), whereas the intensity of low-energy phosphorescence increases with the concentration of anthracene and, as it is seen in Fig.3c its 0-0 transition at 14892 cm^{-1} is the most intense in the total phosphorescence spectrum for the crystal of 1 % mol of anthracene. Thus it is clear that this phosphorescence is of anthracene origin, whereas the high-energy phosphorescence originates in acridine molecules.

The decay time of delayed fluorescence spectrum of mixed crystals with 0.02 and 0.1 %mol of anthracene is, at $T=1.7$ K, equal to 15 ms,

roughly a half of the decay time of acridine phosphorescence dominating in these crystals. In crystal with 1 % mol of anthracene where the anthracene phosphorescence dominates (with $\tau=40$ ms at 1.7 K) the decay time of delayed fluorescence is longer and has the value of 18 ms, also roughly a half of phosphorescence decay time. This and the quadratic dependence of the delayed fluorescence intensity on the exciting light intensity point to the triplet-triplet annihilation as the mechanism responsible for the appearance of delayed fluorescence. At low temperatures, when triplet excitons are efficiently trapped the triplet-triplet heteroannihilation between trapped and mobile triplet excitons takes place. In the case of heteroannihilation on acridine trap the acridine S_1 state is populated and subsequently the excimer of acridine is formed, the delayed fluorescence has excimeric character. When the heteroannihilation occurs on anthracene molecule the created singlet exciton can be also localized on anthracene molecule because anthracene form traps for singlet excitons. In this case the spectrum of delayed fluorescence should resemble the spectrum of anthracene fluorescence shown in Fig.2. The total spectrum of delayed fluorescence is obviously composition of the both above mentioned spectra and its shape can vary with the changes in population of different traps. This explains our observation of changes of delayed fluorescence spectra in crystals of different anthracene concentration (Fig.3).

Preliminary investigations of the high-resolution phosphorescence spectra of acridine as well as of anthracene reveal a 'doublet' structure, the separation between lines is in both cases equal to 42 cm^{-1} . This means that there are two shallow traps of acridine and two deep traps of anthracene origin. The presence of pairs of traps reflects the crystal structure. Anthracene molecule can form two various traps depending on the pair to which a particular molecule belongs to (a pair A with intermolecular distance $d=3.5\text{\AA}$, or pair B with $d=3.7\text{\AA}$). Similarly the acridine molecule can form two various traps localized at pairs A and B.

The intensity of acridine phosphorescence decreases at increasing temperature and disappears at $T=15\text{ K}$. This is the ordinary behavior of emission from shallow traps that are thermally depopulated at elevated temperatures. Anthracene forms deep traps that are depopulated at

higher temperatures - the phosphorescence of anthracene disappears at $T=80$ K. All phosphorescence spectra as well as the phosphorescence excitation spectra of mixed crystals (singlet-triplet excitation, two Davydow components at energies 15752.9 and 15821.0 cm^{-1} identified) are well structured and have 'molecular' character.

It is obvious that all above - mentioned observations are clearly ruling out the possibility of the formation of either triplet excimers or anthracene - acridine exciplexes in chemically mixed crystals under considerations.

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