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B. Kozankiewicz^a, J. Prochorow^a, C. Corvaja^b & A. L. Maniero^b

^a Institute of Physics, Polish Academy of Sciences, P1-02668,
Warsaw, Poland

^b Department of Physical Chemistry, University of Padova, I-35131,
Padova, Italy

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PHASE TRANSITION OF TCNB-NAPHTHALENE CRYSTAL PROBED BY THE CHANGES OF DOPANT EMISSION

B. KOZANKIEWICZ, J. PROCHOROW,
Institute of Physics, Polish Academy of Sciences,
Pl-02668 Warsaw, Poland.

C. CORVAJA and A. L. MANIERO
Department of Physical Chemistry, University of Padova,
I-35131 Padova, Italy.

Abstract Optical spectroscopic studies of single crystals of tetracyanobenzene - naphthalene doped by pyrene were performed within the temperature range around the "order-disorder" phase transition of the host crystal at 73 K. It was established (by the use of phosphorescence and EPR studies) that the geometry of pyrene trap is much different in a low and high temperature phases, thus being sensitive probe of a change of host crystal structure. Activation energy and rate constant describing reorientation of trap structure were obtained.

INTRODUCTION

Tetracyanobenzene (TCNB) - naphthalene (N) complexes form mixed stack charge-transfer (CT) crystal, whose structure consists of stacks where acceptor (TCNB) and donor (N) molecules alternate with each other with their planes being nearly parallel.¹ Characteristic feature of this crystal structure is rigid location of TCNB molecules, favoured by the dipole-dipole interactions between the cyano groups of the neighbouring acceptors which belong to nearest stacks, and a rather loose bonding of N molecules which are disordered between two sites. Earlier experimental and theoretical studies have shown that the "order-disorder" phase transition at $T_c = 73$ K is due to the activation of a large amplitude libration of N molecules between these sites in a double potential well, with rotation axis perpendicular to the molecular planes.²⁻⁵

The dynamic behavior of TCNB-N crystal was also studied with the aid of probe molecules. The examples are previous EPR and ENDOR studies⁶⁻⁸ of TCNB-N crystal doped with pyrene (P) which replaces N

molecules and creates traps for triplet excitons. It was shown that two different pyrene traps, T_1 and T_2 , are present. Trap T_1 which dominates for temperatures above T_c , has CT character $\approx 16\%$ and the long axis of pyrene is directed along the crystal axis b. Trap T_2 can be populated only at temperatures below T_c ; it is nearly completely localized on pyrene molecule (CT character $\approx 0\%$) and occupies two different sites where an angle between long axis of pyrene and crystal axis b is either $+40^\circ$ or -40° .

In the present work we have undertaken detailed optical and EPR studies of emission from pyrene traps in the TCNB-N crystal for temperatures around T_c with the aim to get deeper insight into the nature of T_1 and T_2 traps and into the dynamics of reorientation of the host crystal.

RESULTS AND DISCUSSION

The fluorescence and phosphorescence spectra obtained at 5 K with an excitation to the S_1 state of the host are given in Fig.1a and they closely resemble emission spectra of the pure TCNB-N crystal.¹⁰ The only difference is a structured pyrene-like phosphorescence appearing at low-energy side of the host phosphorescence. In contrary, the fluorescence and phosphorescence spectra of TCNB-P trap are clearly visible under a direct excitation to the trap states - Fig.1b. It can be easily concluded from the spectra under consideration, that excited singlet and triplet states of TCNB-P form deep traps, with depths of ≈ 5000 and 4500 cm^{-1} , respectively.

The emission spectra of TCNB-P trap for temperatures 60 and 80 K are presented in Fig.2. Between these two temperatures, within the narrow 62-73 K range, the intensity of phosphorescence decreases by more than one order of magnitude and it is followed by shortening of the phosphorescence decay time, from 670 ms at 60 K to 28 ms at 73 K. At temperatures above 73 K a new phosphorescence appears and it clearly dominates at 80 K. This phosphorescence band is much broader and has much lower intensity than that at 60 K. It has long decay time - 410 ms. Such a phosphorescence behaviour suggests that below (60 K) and above (80 K) the T_c temperature, it originates from two different traps (with different photophysical properties). The

EPR studies show that with the temperature increase, within the same range (60-70 K), the intensity of signals originating from the low-temperature trap, T_2 , strongly decreases whereas that from

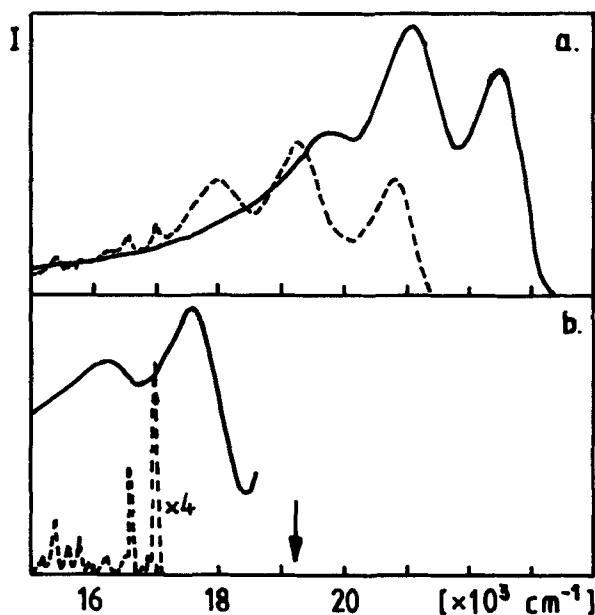


FIGURE 1 Fluorescence (—) and phosphorescence (---) spectra of P doped TCNB-N crystal obtained at 5 K under the (a) - 27350 and (b) - 19250 cm^{-1} excitations.

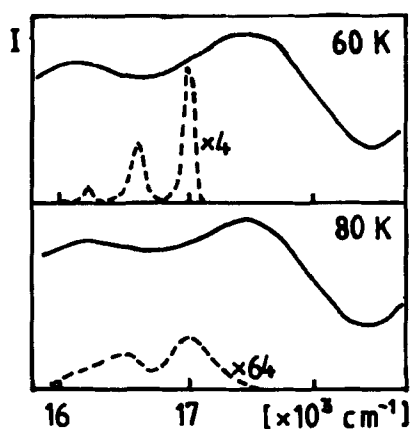


FIGURE 2 Fluorescence (—) and phosphorescence (---) spectra at 60 and 80 K obtained with 19250 cm^{-1} excitation.

high-temperature trap, T_1 , increases. Thus the conclusion, that excitation is transferred between these two traps, gathered either from EPR and/or optical studies is self-consistent.

The rate constant describing depopulation of T_2 trap can be obtained from the Arrhenius-type temperature dependence of phosphorescence decay time (within the 62-73 K range) and such a procedure gives $k=6\cdot 10^{12}\exp(-1350[\text{cm}^{-1}]) [\text{s}^{-1}]$. An intriguing is very high value of pre-exponential factor. An explanation based on thermal depopulation from shallow to deeper trap via the host crystal excitonic band can be easily ruled out, due to the depth of traps. Thus, we believe that sub-picosecond process leading from trap T_2 to trap T_1 , over the 1350 cm^{-1} barrier can be related to the reorientation of pyrene molecule from geometry characteristic for T_2 to geometry of T_1 , induced by a dynamic behaviour of the host crystal structure at temperatures just below the phase transition (when librations of naphthalene molecules are being activated).

To our best knowledge, the present work is the first optical detection of the "order-disorder" phase transition in the molecular crystals of CT complexes.

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