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MIGRATION OF SINGLET AND TRIPLET EXCITONS IN CHARGE -TRANSFER CRYSTALS

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Abstract Single crystals of some charge-transfer (CT) complexes were studied by optical techniques, within the temperature range 4.2-300 K, to gather information relevant to the dimensionality and self-traping of singlet and triplet excitons. Mobile singlet excitons were observed above 100 K when the self-trapping energy was overcome. Activation energy of the mobility of triplet excitons was found to be dependent on their CT character. This dependence confirms the self-trapping origin of the low temperature traps. 1D hopping model describes motion of triplet excitons whereas 3D model referres to migration of singlet excitons. Mobility of singlet and triplet excitons is considerably slowed down in the TCNB-DMN crystal, most probably because of orientational disorder of the donor molecules which leads to a dispersive-like character of exciton motion.

INTRODUCTION

Weak (mixed-stack) charge-transfer (CT) crystals have very characteristic structure with the donor and acceptor molecules alternating along the stack direction, having molecular planes approximately parallel. Such a crystal structure should lead to a quasi one-dimensional (1D) propagation of excitons. Creation of the excited CT state is connected with a complete or partial transfer of the electron from the donor to the acceptor molecule. The optical excitation is therefore expected to induce distortion of a lattice in the neighborhood of excited CT complex. This distortion should decrease the energy and self-traps the exciton. Exciton motion, frozen at low temperatures, should be thermally activated at higher temperatures, with the activation energy of mobility dependent on the CT character of considered excitons.

It was the purpose of this contribution to perform optical spectroscopic and kinetic studies (in the 4.2-300 K temperature range) of some CT crystals , with the aim to gather the experimental data relevant to the problem of self-trapping and

dimensionality of exciton motion. The following systems were studied: tetracyanobenzene - biphenyl (TCNB-B),[1] TCNB - hexamethylbenzene (TCNB-HMB),[1] pyromellitic dianhydride - phenanthrene (PMDA-P)[2] and TCNB - 2,3-dimethylnaphthalene (TCNB-DMN) doped with anthracene. The migration of singlet and triplet excitons were studied from the kinetic data analysis of the host crystal fluorescence and delayed fluorescence (originating from triplet-triplet annihilation) as a function of the dopant concentration, respectively.

MIGRATION OF SINGLET EXCITONS

Singlet excitons in the studied CT crystals are characterized by almost full transfer of electron from the donor to the acceptor molecule and thus the CT characters (c_1^2) of singlet excitons are ≈ 1. Migration of singlet excitons was studied by measuring the host-guest transfer rate from the decay of host fluorescence (under a pulse excitation condition) for the crystals of PMDA-P and TCNB-DMN doped with different concentrations of anthracene. Anthracene (A) has lower ionization potential than the donor molecules of the above host crystals and thus the acceptor-A complex creates deep supertrap for singlet excitons. The host-guest excitation transfer rate in the case of PMDA-P crystal (as well as in the two other previously studied crystals, TCNB-naphthalene doped with A [3] and TCNB-B doped with TCNQ [4]) was found to be practically temperature-independent below 100 K and being continuously increasing at higher temperatures. Such behavior reflects the self-traping of excitons at low temperatures and their thermally activated migration above 100 K. The simple kinetic model with the time-independent host-guest transfer rate describes the exciton migration and points to the 3D migration model. The activation energies, obtained in this work and also taken from two other papers, where the same experimental approach was used, are collected in Table 1.

TABLE 1 Activation energies (ΔE) of the mobility of singlet excitons.

HOST CRYSTAL	DOPANT	ΔE [cm^{-1}]	Ref.
TCNB-N	A	380 ± 40	3
TCNB-B	TCNQ	300 ± 35	4
PMDA-P	A	380 ± 70	2
TCNB-DMN	A	380±50	this work

In the case of TCNB-DMN crystal, for the first time studied in this work, the host-guest transfer rate increases only above 160 K, i.e. at higher temperature than in the other CT crystals.[5] Such observation is consistent with the prediction that the TCNB-DMN host crystal represents a system with disorder. The donor molecules, DMN, may be differently oriented in respect to the acceptors, TCNB. Orientational disorder was already observed and studied in the single crystals of DMN where dispersive-like exciton migration was shown to dominate at low temperatures.[6]

MIGRATION OF TRIPLET EXCITONS

The lowest excited triplet states of the CT complexes can have CT character (c_1^2) between 0 and 1, depending on the relative energy of CT and local triplet states. In the present work we concentrate on the crystals with high c_1^2. The behavior of exciton migration was deduced from the analysis of triplet-triplet annihilation, experimentally followed by the decay of delayed fluorescence.[1,2] Experimentally detected decays of delayed fluorescence were fitted by the theoretical expressions predicted for different models of triplet-triplet (T-T) annihilation. The most symmetrical residual plot and the lowest value of the chi-square pointed to the best model at every temperature.[1] The present approach is alternative to studies by EPR techniques.[7]

Triplet excitons were trapped at low temperatures and the rigid pairs of triplets contributed to T-T annihilation. Triplet excitons were mobile at higher temperatures and their migration was well described by the 1D, thermally activated hopping model.[1] The obtained activation energies of exciton hopping are collected in Table 2.

TABLE 2 CT characters (c_1^2) and activation energies (ΔE) of the mobility of triplet excitons.

CRYSTAL	c_1^2	ΔE [cm^{-1}]	Ref.
TCNB-B	0.5	360 ± 60	1
		250 ± 80	8
PMDA-P	0.76	360±80	2
TCNB-HMB	0.9	650±100	1

These data and the activation energies obtained in the previous EPR studies [8] show, at least qualitative, relationship between the CT character of triplet excitons and the activation energy of their motion: the bigger is c_1^2 - the higher is activation energy.

Moreover, this dependence is a good confirmation of the self-trapping origin of low temperature traps.

In the case of TCNB-DMN crystal a more complicated behavior is observed. Within the temperature range 4.2-70 K, the best fit is obtained when the decay of delayed fluorescence is approximated by the $I_{DF}(t) \propto t^{-\alpha}$ dependence, where α changes from 0.8-0.9 at 4.2 K to 1.7-1.9 at 70 K.[5] The low temperature dependence corresponds to that predicted for annihilation of triplets which are localized on traps.[1] The dependence at 70 K is close to $I_{DF}(t) \propto t^{-2}$, which is predicted for the simple 3D annihilation model.[1] A lack of temperature range with domination of 1D hopping model may be related to orientational disorder of the donor molecules, which slows down exciton mobility. The migration of triplet excitons in TCNB-DMN crystal can not be studied by the presented optical method for temperatures above 80 K, because of domination of thermal delayed fluorescence, which originates from the direct $T_1 \rightarrow S_1$ thermal activation.[5]

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