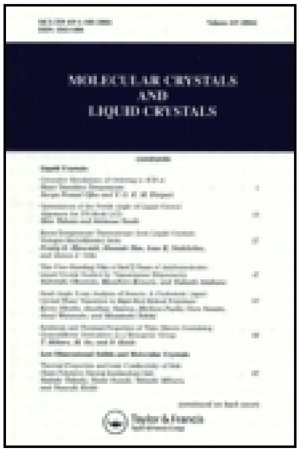

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Peculiarities of Radiative Recombination in Poly-N-epoxypropylcarbazde Doped With Polymethine Dyes

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Peculiarities of Radiative Recombination in Poly-N-epoxypropylcarbazole Doped With Polymethine Dyes

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Processes of charge carrier photogeneration and recombination are investigated in films of poly-N-epoxypropylcarbazole (PEPC) doped with polymethine dyes. It is presumed, that the cause of growing the recombination luminescence intensity in external electric field is connected with increase of efficiency of radiative recombination stimulated by captured electrons from photogenerated excitons.

Keywords: electron-hole pairs; excitons; photoconductivity.

INTRODUCTION

The samples of sandwich structure are usually used for experimental investigations of electroluminescence (EL) in polymer films of amorphous molecular semiconductors (AMS)[1]. Field injection of charge carriers from contacts into AMS film volume can be rather effective for appropriate electric contacts. During recombination EL in electric field charge carriers emerge from contacts, drift within the AMS film volume, meet and recombine in recombination centers under the light influence. During this process as the recombination centers act molecules distinguishing from ones, which take part in charge carriers transport. An efficiency of recombination EL depends on the conditions of carriers injection from contacts, on their transition from transport molecules to ones being recombination centers as well as on the relation between probabilities of radiative and nonradiative degradation of excited state of recombination center. Besides, the history of the sample produces an effect on recombination EL. In particular, strengthening of recombination EL upon visible light illumination was observed in the present work for the samples being previously irradiated with UV light. Processes of photogeneration, recombination and strengthening of the radiative recombination of charge carriers in the films PEPC doped with 1,2,3,1',3',3'-hexamethylindocarbo-cyanine tetrafluoroborate (HIC) are studied in the present work Choice of PEPC layer for holes transport was determined by high efficiency of holes transport through carbazole rings[2]. On the other hand, HIC were chosen as the recombination and photogeneration centers because absorbtion and luminescence bands exist in visible and near IR parts of spectrum depending on molecule structure and also due to a high quantum yield of luminescence. High valence states of HIC are energetically close to high valence orbital of carbazole[3], therefore hole transitions from PEPC carbazole nucleus into valence molecular orbitals of HIC molecules and in opposite direction can take place.

Samples and Experimental Methods

The samples for investigations were prepared either as a structure with free surface: quartz substrate - PEPC+Nmas.%HIC, or as a sandwich structures: Al-PEPC+Nmas.%HIC-SnO_2, where N=0.1-15 mas.%. For AMS films based on PEPC Al and SnO_2 contacts are blocking under the positive polarity on Al electrode[2]. In the samples of sandwich structure dependencies of following parameters versus electric field (E) and intensities I_1 and I_2 for two wavelengths λ_1=380 nm and λ_2=540 nm were measured: i) photocurrent density (j_{PH}); ii) photoluminescence intensity; iii) concentration (Q) of charge carriers appearing in electrically short-circuited sample during a time t_1 of its illumination with monochromatic light and emerging into accumulating contacts; charge carriers motion was observed under applied electric voltage after time interval t_2 afterwards light pulse end; iv) intensity of recombination luminescence (I_E) during the time Q of measurements. In accordance to developed and described in[2,4] method, Q is determined by following expression: $Q=\int_0^\infty dt\{i_2(t)-i_1(t)\}/qSL$, where t=0 corresponds to switching on the electric field, q is the electron charge, S and L are the area and the thickness of the AMS film positioned between the contacts respectively, $i_1(t)$ is the current of charging of an electric capacity of short circuited sample during the time t_1+t_2 in darkness, $i_2(t)$ is the same current for the sample previously being illuminated with monochromatic light in short circuited state during time interval t_1 and than held in darkness during time interval t_2. A change of Q after the electric field application was calculated according to the following relation: $Q_t(t)=\{i_2(t)-i_1(t)\}/qSL$.

Results of Experiments

The photoconductivity for light of wavelengths λ_1 and λ_2 was observed in all samples Al-PEPC+Nmas.%HIC-SnO_2 with sublinear dependency of photocurrent on I_1, I_2 and L. Graphic $j_{PH}(E)$ is linear in coordinates $lg\ j_{PH}$ versus $E^{1/2}$. The dependencies I_E/I_{Emax} (curves 1-3) and Q_t/Q_{tmax} (curves 1'-3') normalized to respective maximum values at given E versus time t after electric voltage application are plotted in Fig.1. The correlation between the dependencies $I_E(t)$ and $Q_t(t)$ is obvious. L growth upon constant or decreasing E involve both a shift of I_{Emax} and Q_{tmax} toward greater t and a growth of irradiation duration and Q measurement.

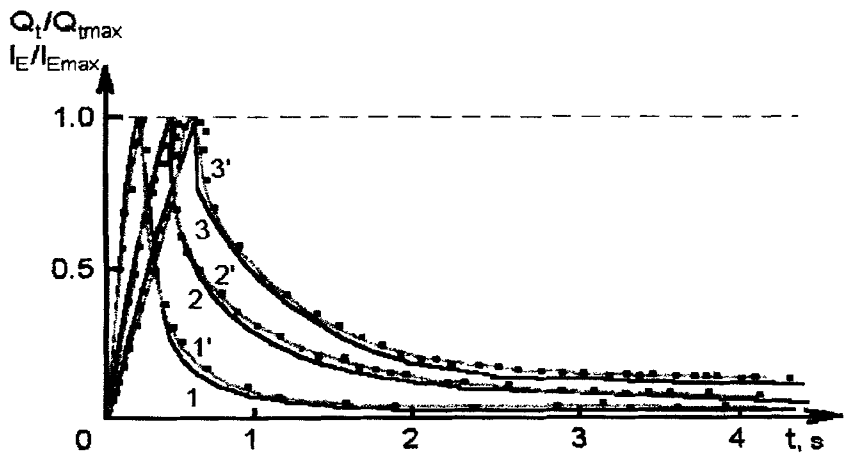

FIGURE 1 Kinetics of recombination luminescence (1-3) and emerging of photoinduced volume charge into contacts (1'-3') in the sample Al-PEPC+1 mas.% HIC-SnO_2 (L=1.3 μm) after its illumination with light with λ_2 during t_1 = 30 s, holding in darkness during t_2=30 s and application of the external electric field E=2.8·10^8 V·m^{-1}(1, 1'), 1.7· 10^8 V·m^{-1} (2, 2'), 7·10^7 V·m^{-1} (3, 3).

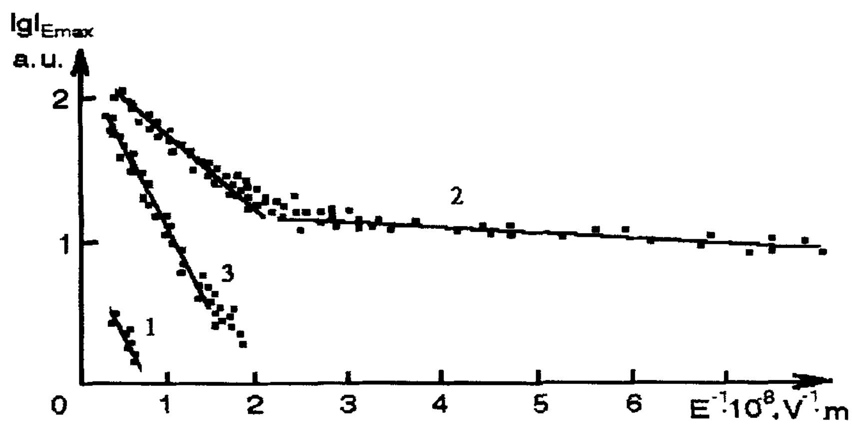

FIGURE 2 Dependencies I_E(E) in the sample Al-PEPC+0.5mas.%HIC-SnO_2 (L=1.1 μ m) for t_1= 30s, t_2 =10 s.

Curve 1 in Fig.2 presents a graphic of dependency lgI_{Emax} versus E^{-1} measured in the sample, which was not illuminated with light λ_1 longer than 24 hours. Curve 2 presents analogous graphic for the sample, which was illuminated with light λ_1 before electric field application. Curve 3 was obtained in the same sample after curve 2 registration upon illumination with light λ_2. As it follows from the results shown in Fig.2, previous illumination with light with λ_1 involves significant I_E growth in the next cycles of the samples illumination with light with λ_2 and I_E measurements. We should note at once that in chosen coordinates the approximation of experimental dependencies $I_E(E)$ by linear dependencies is possible.

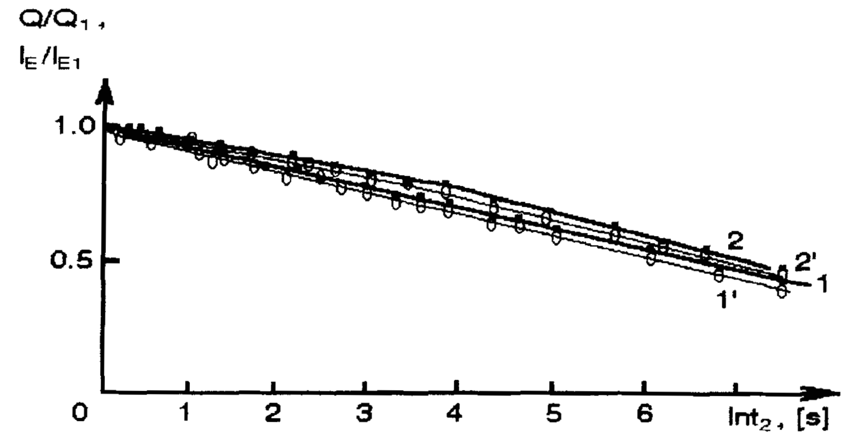

FIGURE 3 Dependencies of Q (1, 2) and I_E (1', 2') versus t_2 in the sample Al-PEPC+1 mas.% HIC-SnO_2 (L=1.3 μ m) after its illumination with light with λ_1 (1, 1') and λ_2 (2, 2').

Graphs of dependencies Q/Q_1 versus lnt_1 (curves 1,2) and I_{Emax}/I_{Emax1} versus lnt_2 (curves 1',2') are presented in Fig.3, where Q_1 and I_{Emax1} are the respective values for t_2=1s. In chosen coordinates the experimental results could be approximated by linear dependencies with close tangents of inclination angle. These dependencies measured for illumination time t_1=30 s, where $Q(t_1)$ and $I_E(t_1)$ have a saturation region. Dependencies $Q(t_1)$ and $I_E(t_1)$ are similar. Linear character and equal slope of dependencies Q/Q_1 on lnt_2 and I_{Emax}/I_{Emax1} on lnt_2 (see Fig.3) allows to conclude that after AMS film illumination with light with

λ_1, λ_2 EHPs appear, where holes and electrons are distributed as an isolated pairs with distance r between charges and distribution function $f(r)$. If electric voltage is applied to the sample after time interval t_2 afterwards illumination switching off, then charge carriers in EHP become mobile and could recombinate with light. Process of radiative recombination is analogous to the process of charge carriers tunneling through potential barrier Δu, because dependencies $\lg I_E$ on E^{-1} could be approximated by linear dependencies and dependency I_E on E satisfies the analytical expression: $I_E \sim \exp\{-8\pi(2m^*)^{1/2}\Delta u_1^{3/2}/3qhE)$ where m* is the effective mass of charge carrier, h is the Plank constant.

Additional investigations of the reasons of long live EHP appearance, mechanisms of electron trapping after collapse of photogenerated excitons as well as these electrons influence on the probability of charge carriers radiative recombination are necessary to precise mechanism of the recombination EL strengthening under UV-light influence, which was discovered at the present work. However, even the results in the present work obtained allows to make supposition that in PEPC+Nmas.%HIC after illumination with light from near UV range the active centers appear consisting of entrapped electrons from photogenerated excitons. These centers effectively effect on the probability of radiative recombination of charge carriers. Mechanism of such influence could be connected with change of velocity of singlet-triplet transitions in recombinating pairs of charge carriers.

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