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Radiative recombination of PVC/C₆₀ molecular complexes with radiation-induced damages

E.S. Kobus¹, O.P. Dmytrenko¹, N.P. Kulish¹, Yu.I. Prylutskyi², N.M. Belyi¹, V.G. Syromyatnikov³, S.L. Studzinskyi³, M.A. Zabolotnyy³, D.A. Gryn'ko⁴, D.V. Shchur⁵, V.V. Shlapatskaya⁶

Taras Shevchenko Kyiv National University, Departments of Physics¹, Biophysics² and Chemistry of High-Molecular Compounds³, 64, Volodymyrska str., 01033 Kyiv, Ukraine

⁴V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, 45, prospect Nauky, 03028 Kyiv, Ukraine

⁵Institute for Problems of Materials Science, NAS of Ukraine, 3, Krzhyzhanovsky str., 03142 Kyiv, Ukraine

⁶Institute of Physical Chemistry, NAS of Ukraine, 31, prospect Nauky, 03028 Kyiv, Ukraine

Abstract. The relaxation processes of electronic excitations in the films composed from a mixture of the amorphous semiconductors of polyvinylcarbazole and C₆₀ fullerenes (PVC/C₆₀) with different contents of nanocluster molecules and beyond the threshold electron irradiation are studied. It is shown that, in the entire range of the concentrations of C₆₀ molecules, for which the molecular disperse state of a mixture retains, the complexes with the charge transfer due to the photogeneration of electron-hole pairs are observed in the PVC/C₆₀ films. The photoluminescence spectra indicate the presence of both the molecular emitting transitions and the recombination luminescence caused by the electron transfer in the composition of excitons from the matrix to impurity fullerenes. Depending on the content of C₆₀ molecules, the photoluminescence spectra are substantially reconstructed, reflecting the changes in the electron structure of molecular complexes. The nature of these changes retains with the introduction of radiation-induced damages under high-energy electron irradiation with an absorbed dose of 3.0 MGy.

Keywords: electronic excitation, photogeneration, photoluminescence, complexes with the charge transfer, electron irradiation.

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1. Introduction

The expansion of the use of amorphous organic photo-semiconductors as the photoreceptors, the media for the optical record of information, is possible with the sensitization of the photoconductive effect. It is achieved by the introduction of dopants which absorb visible light and are able to the effective photogeneration of charge carriers. As the amorphous molecular semiconductors, the carbazole-containing polymers on the basis of polyvinylcarbazole (PVC) and poly-N-epoxypropyl-carbazole with the *p*-electron associations localized in the separate groups are usually used. Since the macromolecules of these vinylaromatic polymers with electron-donor carbazole groups absorb in the near UV-range, their sensitization is carried out by the *p*-type impurities, compounds with the intramolecular charge transfer or by dyes which expand the absorption to the visible and IR regions [1-4]. The centers of the photogeneration of charge carriers in the case of doping

organic electron acceptors are the intermolecular complexes with the charge transfer, which are formed with electron-donor *p*-groups. With the introduction of compounds with the intramolecular charge transfer into the amorphous semiconductors, such centers are the doped molecules [5-7]. After the light absorption by the photogeneration centers, the Coulomb connected electron-hole pair appears, whose hole is localized at the carbazole nucleus of photoconductive polymers, and the electron is localized on the impurity molecules. In future, the charge carriers in the pair either are separated or recombined. The recombination of charge carriers has the emitting nature. The transport of electrons and holes, which occurs as a result of the tunneling junctions between the local levels of molecules, contributes to the separation of charges. The transfer of electrons and holes occurs between the lower unoccupied molecular orbitals of adjacent acceptor molecules and the high occupied molecular orbitals of donor molecules, correspondingly [8-9].

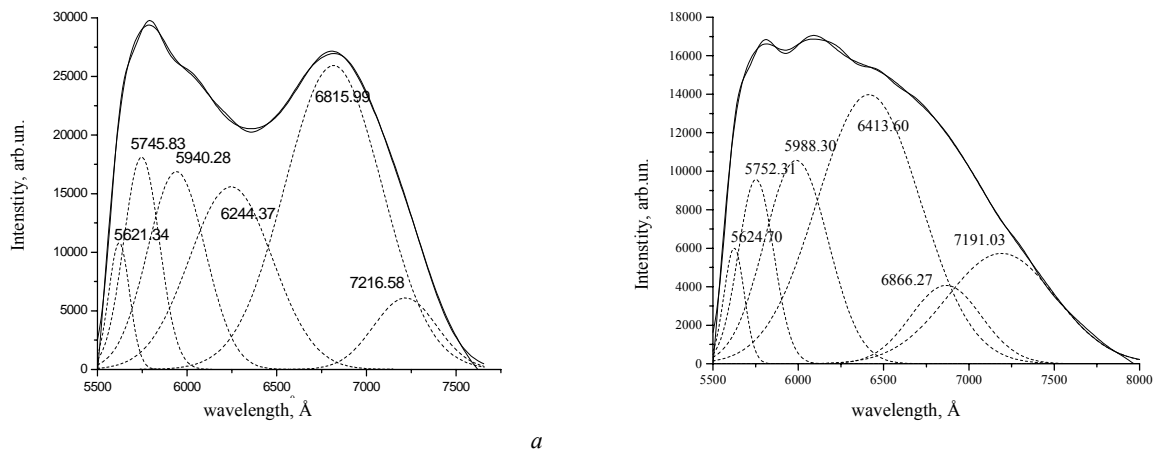


Fig. 1. Photoluminescence spectra and their decomposition into components for the PVC films in the initial state after spraying (a) and electron irradiation with an absorbed dose of 3.0 MGy (b) ($T = 77$ K, Si(100) substrate, the thickness is 100 nm, $\lambda = 514.5$ nm, $E_e = 1.8$ MeV).

The radiative recombination of photogenerated electron-hole pairs in the polymer-acceptor complexes is superimposed on the photoluminescence caused by the emitting transitions of photoexcited molecules into the ground state. Therefore, the processes of energy relaxation of electronic excitations depend on the density function of electronic states of the formed complexes, i.e. the local states of molecules and their changes as a result of intermolecular interactions, including the appearance of the local levels related to the conformational transformations of molecules [10].

Fullerenes are strong electron acceptors that contribute to a sharp increase in the photogeneration of the molecular complexes created by the aromatic donor molecules of carbazole polymers with fullerene molecules. The photogeneration process with the sensitization by fullerenes is achieved as a result of the photoinduced electron transfer inside the chain of the polymer in the composition of an exciton to a fullerene molecule [11]. The recombination of a Coulomb connected electron-hole pair is accompanied by the relaxation of the electronic excitation. However, its mechanism is studied insufficiently under the beyond threshold ion irradiation.

The purpose of this work is the study of the dynamics of the relaxation of electronic excitations of complex-formed π -conjugated donor vinylcarbazole polymers with their doping by the acceptor molecules of C_{60} fullerenes after the radiation-induced damages created by the high-energy electron irradiation with different absorbed doses.

2. Experimental

The mixture of the semiconductor PVC polymers and C_{60} fullerenes was deposited in vacuum to the polished surface of silicon with crystallographic orientation (100)

by evaporating both components of two sublimation sources at different temperatures. The surface of silicon was preliminarily cleaned with argon ions, and the sublimation sources for their degassing before the spraying were subjected to the multihour annealing at a temperature of 423 K. The thickness of the homogeneous films of PVC/ C_{60} mixture was ~ 100 nm.

Emitting transitions were investigated by the spectra of photoluminescence with the excitation by an argon laser ($\lambda = 514$ nm) at the temperatures of liquid helium and nitrogen. As the spectroscopic instrumentation, a diffraction monochromator MDR-3 was used. The registration of spectra was performed by a photodetector FEU-62 by the method of accumulation.

Irradiation was conducted in the output channel of a linear electron accelerator ILU-6. The absorbed dose was 3.0 MGy with the energy of bombarding electrons $E_e = 1.8$ MeV.

3. Results and discussion

The pumping with an argon laser leads to the appearance of the wide structural maximum of photoluminescence, whose position is in the region of (550–750) nm (Fig. 1). An analogous band in the luminescence PVC spectrum was observed also in other works [12-14], although its maximum is displaced, by depending on a state of the polymer. This band is connected with the generation of triplet excitons in the macromolecules and their migration along the polymer chain with the subsequent deactivation of the energy of electronic excitations by photooxides [15-16]. During the electron irradiation with an absorbed dose of 3.0 MGy, the structure of the phosphorescence band disappears. The maximum near 682 nm substantially decreases, which leads to a reconstruction of the long-wave part of the spectrum.

It is possible to assume that the phosphorescence extinction is a consequence of the decrease of radiative recombination due to the appearance of the links between the π -conjugated nuclei along PVC molecules that contribute to the migration of T-excitons.

With a low content of C_{60} fullerenes (0.5 wt %), the spectrum of photoluminescence changes as a consequence of the increase in its component near 720 nm, while the component of the emission with $\lambda \approx 682$ nm decreases. The short-wave part of the spectrum in this case remains constant (Fig. 2). With a further increase in the concentration of C_{60} fullerenes (1 wt %), the integrated intensity of the peak of photoluminescence increases, its half-width decreases, and its maximum displaces to the position of the emission line (~ 732 nm), which corresponds to the emitting transition caused by Frenkel singlet excitons on the dimeric traps of C_{60} molecules [17].

It is seen that, with increase in the content of fullerenes, the photoluminescence extinction of polymers occurs, which is a consequence of the electron transfer to

fullerenes. The re-emission of the electronic excitation generated in the matrix in the molecules of doping fullerenes occurs with a complex reconstruction of the photoluminescence spectrum. This testifies to the essential intermolecular interaction caused by the formation of complexes with the charge transfer which are responsible for the relaxation of energy excitations.

The aggregation of impurity C_{60} molecules is absent with the selected levels of doping. Therefore, there is the intermolecular excimer emission with the predominance of the impurity emission. In that time, the photoluminescence of the PVC/ C_{60} mixture takes the form characteristic of C_{60} fullerite only in the pre-aggregation state, although, in this case, the intramolecular emission feels the influence of macromolecules of the polymeric matrix.

Photoluminescence spectra of the PVC/ C_{60} mixture are qualitatively changed a little as the temperature decreases to that of liquid helium. However, the emission of polymer molecules noticeably decreases in the range of long wavelengths, which leads to a change

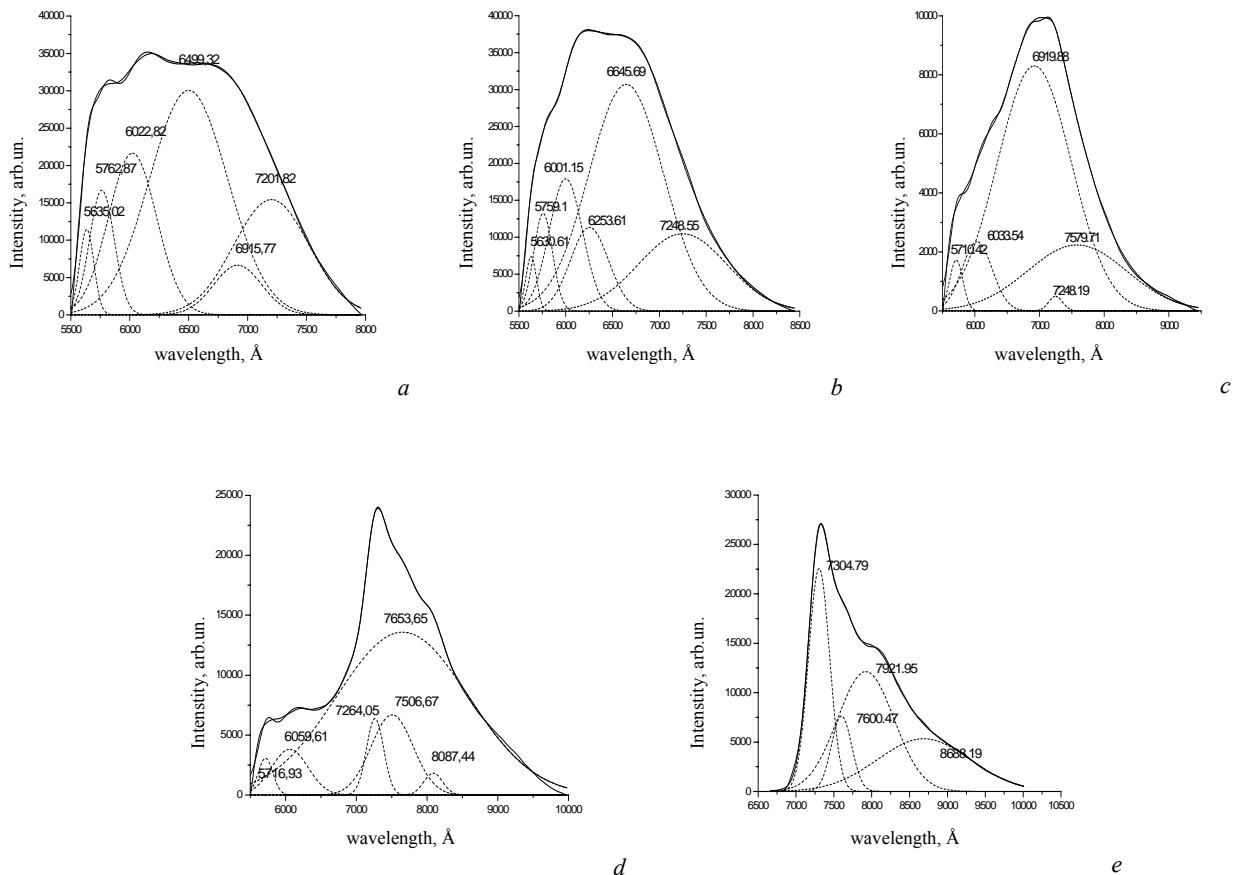


Fig. 2. Photoluminescence spectra and their components for the PVC/ C_{60} films, which contain 0.5 (a), 1.0 (b), 1.5 (c), and 3.0 (d) wt % of C_{60} fullerene, and for the C_{60} fullerene film (e) at $T = 77$ K (Si(100) substrate, the PVC/ C_{60} film thickness is ~ 100 nm, the C_{60} fullerene film thickness is ~ 2 μm , $\lambda = 514.5$ nm).

in the asymmetry of the peak on the comparison with its form at $T = 77$ K (Fig. 3). This behavior of the relaxation of electronic excitations indicates the growth of the interaction between the π -conjugated groups of macromolecules due to the formation of donor-acceptor bonds caused by the presence of fullerenes.

Thus, the mixture of amorphous semiconductor π -conjugated polymers with C_{60} fullerenes is characterized by the formation of the molecular complexes caused by the donor-acceptor intermolecular interaction. Their electron structure changes in the dependence on the content of the doping molecules, which determines the re-emission of the energy of matrix excitations.

Since the molecules of PVC and fullerenes interact between themselves in the mixture, the transport of excitations from PVC molecules to C_{60} ones is effective, which predetermines the extinction of the emission of PVC molecules and its increase near the peak of 732 nm for fullerene molecules.

During the prolonged irradiation of the PVC/ C_{60} mixture by the laser emission, the opposite phenomenon occurs, namely an increase in the intensity of the emission

of PVC macromolecules with the preservable value of photoluminescence connected with the first excited singlet state of C_{60} fullerenes (732 nm) [18]. This means that, with the photoexcitation, the transfer of excitations is possible from C_{60} molecules to PVC ones. Since the emission intensity near the peak of 732 nm remains constant, the energy transfer from the singlet state is impossible. It is assumed that a part of C_{60} molecules after the intercombinational transition from the S_1 state into the T_1 one is in the triplet state. In this state, they create complexes with PVC molecules. With the excitation of C_{60} molecules in the triplet state, the energy transfer from these molecules or from the complexes with such molecules to the polymeric PVC ones becomes possible, which contributes to an increase in their emission.

Figure 4 shows that the accumulation of C_{60} molecules in the triplet state is absent during the beyond threshold electron irradiation. As a result, the emission of PVC molecules decreases.

Consequently, the mechanism of the relaxation of energy excitations in the case of a high concentration of fullerenes with the radiation-induced damages of

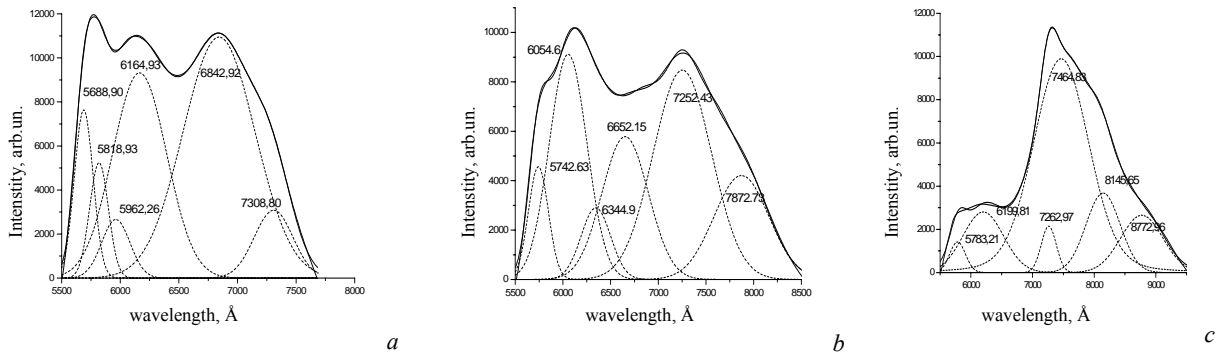


Fig. 3. Photoluminescence spectra and their components for the PVC/ C_{60} films which contain 0.5 (a), 1.5 (b), and 3.0 (c) wt % of C_{60} fullerene at $T = 4.2$ K (Si(100) substrate, the thickness is 100 nm, $\lambda = 514.5$ nm).

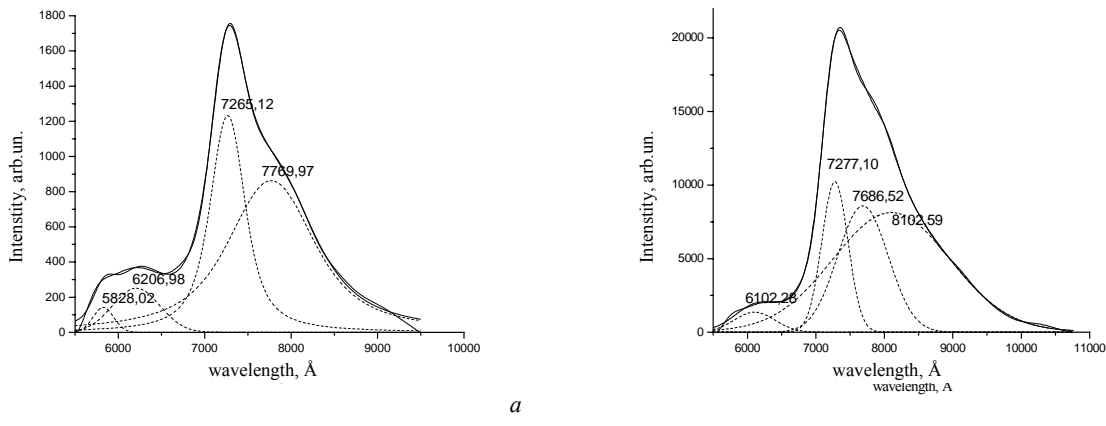


Fig. 4. Photoluminescence spectra of the PVC/ C_{60} films which contain 3.5 wt % of C_{60} fullerene in the initial state of spraying (a) and after electron irradiation with an absorbed dose of 3.0 MGy (b) obtained at $T = 77$ K (Si(100) substrate, the thickness is 100 nm, $\lambda = 514.5$ nm, $E_e = 1.8$ MeV).

molecules does not provide for the possibility of the accumulation of C₆₀ molecules in the triplet states, although such processes are not excluded with a smaller content of fullerenes and other radiation doses.

4. Conclusion

In a homogeneous mixture of the films of the carbazole-containing amorphous molecular semiconductors with C₆₀ fullerenes (PVC/C₆₀), the formation of complexes with the charge transfer is observed. Their presence creates the structure of electronic states, which changes in the dependence on the content of the acceptor C₆₀ dopant. Such changes in the electrical structure lead to different special features of the relaxation of electronic excitations which include both the molecular emitting transitions and the recombination luminescence. The mechanism of the latter provides for the deactivation of electronic excitations as a result of their transfer to fullerene molecules by the migration of excitons on carbazole interacting π -conjugated groups along the chain of polymeric molecules. The same mechanism retains during the beyond threshold electron irradiation of the PVC/C₆₀ mixtures with a high content of fullerenes.

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