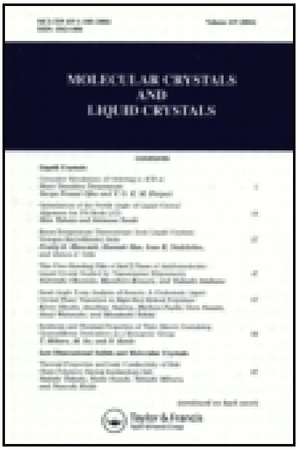

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M. A. Zabolotny [a] , N. P. Kulish [a] , Yu. L. Prylutskyy [a] , Yu. M. Barabash [b] , D. A. Gryn'ko [c] , O. P. Dmytrenko [a] , N. M. Biliy [a] , E. S. Kobus [a] , E. L. Pavlenko [a] , O. P. Olasiuk [a] , U. Ritter [d] & P. Scharff [d]

[a] Kyiv National Shevchenko University, Department of Functional Materials Physics, Kyiv, Ukraine

[b] Institute of Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine

[c] Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine

[d] Technical University of Ilmenau, Chemical Department, Ilmenau, Germany

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Photostimulated Processes in PVK-C_{60} Nanocomposites

M. A. Zabolotny[1], N. P. Kulish[1], Yu. L. Prylutskyy[1], Yu. M. Barabash[2], D. A. Gryn'ko[3], O. P. Dmytrenko[1], N. M. Biliy[1], E. S. Kobus[1], E. L. Pavlenko[1], O. P. Olasiuk[1], U. Ritter[4], and P. Scharff[4]
[1]Kyiv National Shevchenko University, Department of Functional Materials Physics, Kyiv, Ukraine
[2]Institute of Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine
[3]Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine
[4]Technical University of Ilmenau, Chemical Department, Ilmenau, Germany

We studied dependence of the photoluminescence spectra of the PVK-C_{60} nanocomposites synthesized by vacuum evaporation on the fullerene concentration as well as the temperature of the samples. Our experiments show that exposure of the PVK-C_{60} composites to a 514.5 nm irradiation induces reversible changes leading to heterogeneous concentration-dependent modifications of the photoluminescence spectra.

Keywords: amorphous organic molecular semiconductors (OMS); charge-transfer complexes; photoluminescence; PVK-C_{60} nanocomposites

INTRODUCTION

Amorphous organic molecular semiconductors (OMS) are widely used as optical recording media and as elements of optoelectronic devices, since they are characterized by controllable absorption spectra, structural flexibility, substantial light photoconductivity, low dark photoconductivity, as well as by their ability to photogenerate

Address correspondence to E. S. Kobus, Kyiv National Shevchenko University, Department of Functional Materials Physics, Volodymyrska Street, 64, Kyiv 01601 Ukraine. E-mail: kobus_olena@ukr.net

long-lived electron-hole pairs [1–4]. These factors are responsible for the search and study of new polymer compositions, which possess the nonlinear optical and electro-optical properties, suitable for the real applications.

Carbazole-containing amorphous molecular semiconductors on the basis of poly-N-vinylcarbazole] (PVK) and poly-N-epoxypropilcarbazole] (PEPK) are the typical examples of used OMS [2,4]. These materials are doped by the molecular additives, which create [1,2,4] together with the OMS molecules the charge-transfer complexes for the sensitization of the photoconductive effect.

Such complexes broaden the spectrum of light absorption on the one hand, and on the other hand they are the centers of the photogeneration of charge carriers [2,4]. The possibilities of using the dyes as sensitizers of photoconductivity are investigated in detail [2,4]. New possibilities are opened by the use of fullerene additives [2,3,5].

The inertial optical nonlinearity of photo-refractive polymer compositions on the basis of PVK and C_{60} was established by a study of the fullerene impurities influence on the properties of the doped polymers [3]. In the explanation proposed the following unsolved question is still remaining: In what degree the nonlinear effect is dependence on the temperature of the sample, the wavelength, and the intensity of exciting light (i.e., how much these effects have a cooperative nature). This question is natural upon consideration of the distinctive characteristic of sensitizers on the basis of fullerene that is its ability to accept up to six electrons.

With the selection of experimental methods for the study of polymer-fullerene composite interaction it was taking into account that the acceptor sensitizers, which form with the electron-donor carbazole groups of the intermolecular complexes by charge transfer, influence the transfer of energy of the electron excitation. This energy is determined by the interaction between the fullerene and the polymer. The changes in the photoluminescence spectra (PL), caused by the quenching luminescence of carbazole-containing molecules by the fullerenes are characteristic for such intermolecular interaction. This phenomenon is caused by a structural reorganization of polymers and the appearance of structural defects, which influence the migration of the electron excitation energy. With respect to the changes of luminescence in the presence of fullerenes it is possible to obtain the information about the interaction between them [6]. Thus, this work is devoted to the study of the C_{60} fullerene concentration and temperature of sample influence on the PL spectrum of the PVK-C_{60} composite, obtained by the use of vacuum deposition technology. The purpose of the work was the development of new nanomaterials with an optically controlled PL spectrum.

SAMPLES AND EXPERIMENT

In the present work the PL and transmission spectra are studied in the visible range of the spectrum of PVK films, which contain C_{60} fullerenes. The used PVK was synthesized at the Department of Chemistry of Kyiv National Shevchenko University. It was purified employing known procedure [4] and had the molecular weight of $(6–7) \cdot 10^3$ a.u. The purity of C_{60} powder was composed 99, 9%. The concentration of fullerenes in the samples is varied in the range of 0.5 to 3 wt%.

The samples of the composite polymer films with the fullerenes, obtained by the simultaneous evaporation of molecules of both components to the Si (100) support from two separate heaters, placed in a vacuum chamber, were used. The temperature of heating was selected on the basis of the temperature values of the sublimation of each component. Before the evaporation to the support and to remove the molecules of organic solvents the powders of the polymer and the fullerenes were warmed thoroughly for long time in vacuum. The thickness of the films was about 100 nm. The small values of the thickness of the samples, and also the insignificant value of the exciting light intensity are guaranteed the independence of the absorption coefficient of the sample from the film thickness.

PL of PVK-C_{60} films was investigated by temperatures $T = 77$ and 300 K respectively. For the excitation an continuous pumping argon laser ($\lambda = 514, 5$ nm) was used. Power in the beam did not exceed 1 W/cm^2. Power density was regulated by a change in the voltage, applied to the radiated laser. The size of the region of the target illuminating did not change. The halogen incandescent lamp was used for the measuring the transmission spectrum of samples.

RESULTS AND DISCUSSION

PL spectra were defined both for the initial reagents and for their composites. Figure 1 (curve 1) shows PL spectrum of PVK taken at 77 K. There are two distinct maxima – a more intense one around 730 nm and a smaller one close to 620 nm.

It is necessary to note that PL spectrum (Fig. 1, curve 1) is differed essentially from the spectra of the samples, which were prepared both with the aid of watering from the toluene solution and with the use of a procedure of evaporation in an atmosphere of inert gas. This fact can be explained by the assumption that in the process of evaporating the PVK molecules their disintegration to the separate fragments, whose nature depends on the properties of the medium, in which the evaporation occurs (its composition, pressure), takes place. During the

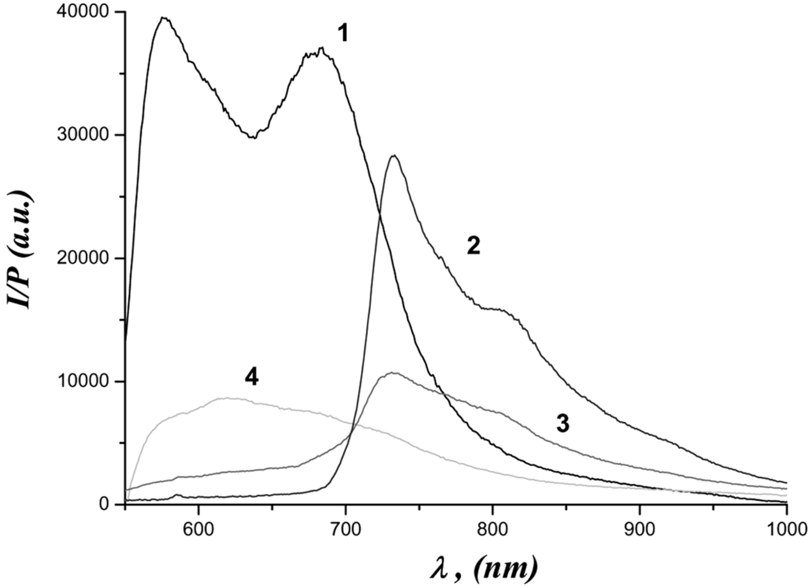

FIGURE 1 Luminescence spectra of evaporated PVK (curve 1), C_{60} (curve 2), and also their composites of PVK + 3% C_{60} (curve 3) and PVK + 0.5% C_{60} (curve 4), excited by the light with the wavelength of 514.5 nm at T = 77 K.

precipitation of the molecule fragments the repolymerization and packing of PVK molecules occurs. It follows that the PVK structure, its optical (and, possibly, rheological) properties depend on the technology of the sample preparation.

PL spectrum of C_{60} fullerenes (Fig. 1, curve 2) also reveals two maxima – a more intense one around 735 nm and a second near 804 nm.

In Figure 1, curves 3 and 4, we provide PL spectra taken at T = 77 K for PVK + 3 wt% C_{60} (curve 1) and PVK + 0.5 wt% C_{60} (curve 2). Comparison of Figure 1, curves 3 and 4, with the data plotted in Figure 1, curves 1 and 2, indicates that the maxima positions in the spectra of C_{60} fullerenes and PVK + 3 wt% C_{60} coincide so that the presence of PVK has a footprint only in the region smaller then 680 nm. By a concentration of 0.5 wt% C_{60} the short wave peak (~620 nm) of PVK remains in the spectrum and it is not recorded as the long-wave. The typical peaks for C_{60} fullerene are not manifested.

The results of analogous measurements carried out at T = 300 K are represented in Figure 2. The analysis of the curves, presented in Figure 1, curves 3 and 4, with the use of the functions, represented

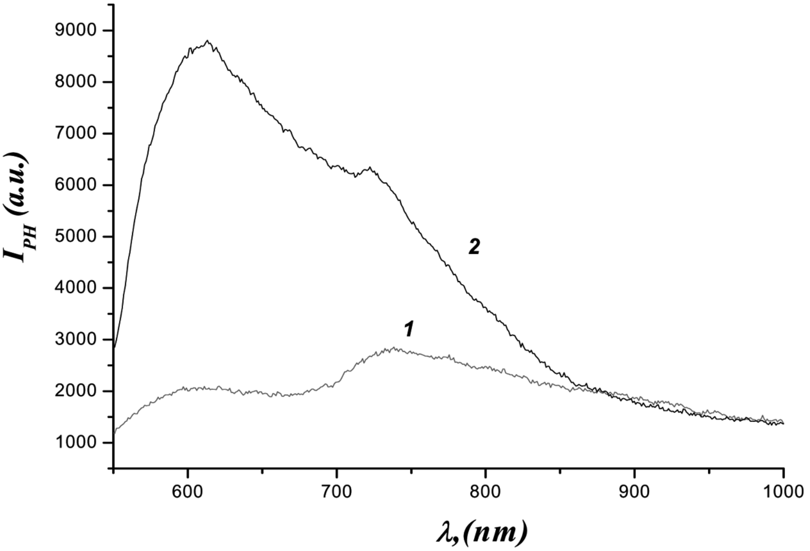

FIGURE 2 PL spectra of the PVK + 3 wt% C_{60} (curve 1) and PVK + 0.5 wt% C_{60} (curve 2) nanocomposites at $T = 300\,K$ ($\lambda_{ex} = 514.5$ nm; $P = 0.7\,W/cm^2$).

in Figure 1, curves 1 and 2, with the aid of the least-squares method showed that it is not possible the curves of Figure 1, curves 3 and 4 to present in the form of the linear combination of curves, presented in Figure 1, curves 1 and 2, with an error that not exceeding 10%. From this it follows that the luminescence of the new compound, which, in our opinion, is the charge transfer complex, introduces the contribution into the spectrum of composite. To the same conclusion (but with error no less than 15%) leads the data analysis, presented in Figure 2 with the use of the PVK and the C_{60} fullerene spectra, defined at $T = 300\,K$. That is formation complexes with the carrier transfer are possible both with room temperature and nitrogen temperature independently of possible changes of crystalline structure formatting fullerites or conformation of PVK molecules. These data show that the luminescence spectrum of the composites substantially depends both on the temperature, and the concentration of the fullerenes. The curves, presented in Figure 3, illustrate the same tendency also. The dependence of the form of the composite luminescence spectra on the concentration of the fullerenes can show the forming of associates (fullerites) from C_{60} during evaporation, the sizes of which depend on the C_{60} fullerene concentration.

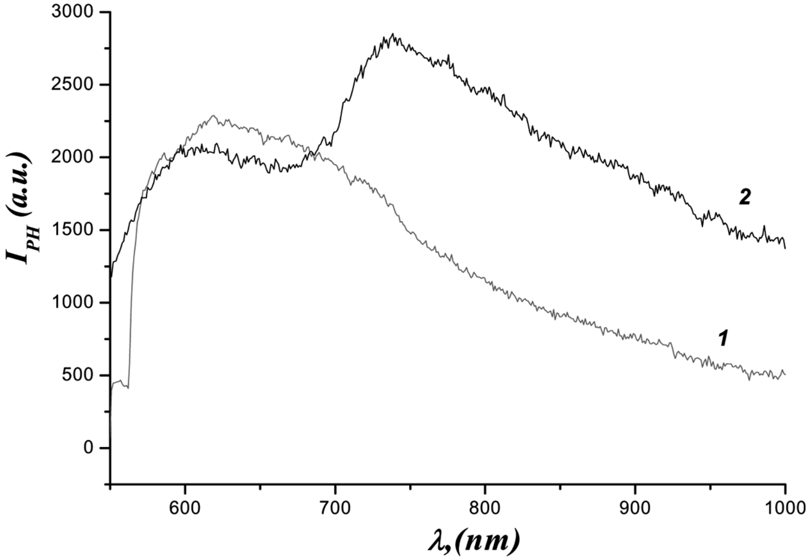

FIGURE 3 PL spectra of the PVK + 0.5 wt% C_{60} nanocomposite at T = 77 K (curve 1) and T = 300 K (curve 2) ($\lambda_{ex} = 514.5$ nm; P = 0.7 W/cm^2).

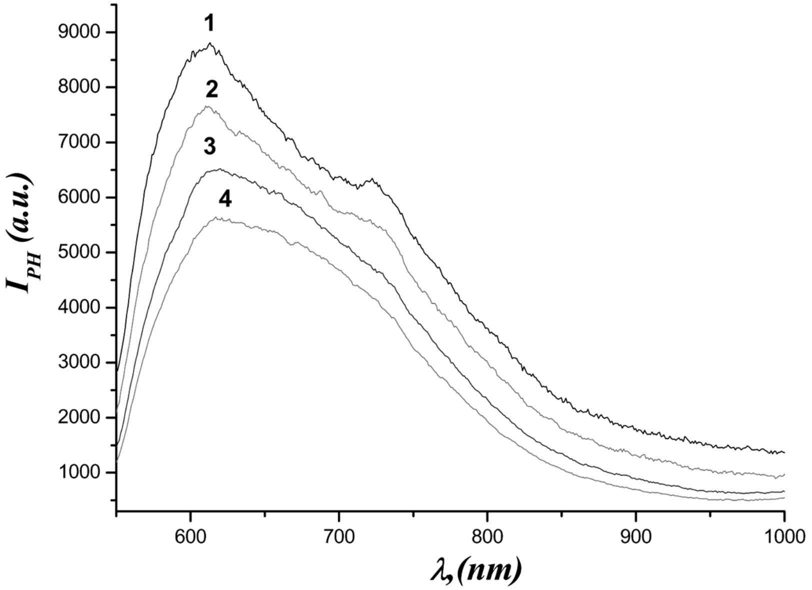

FIGURE 4 PL spectra of PVK + 0.5 wt% C_{60} for different incident light flux densities (P): 1 – 0.4; 2 – 0.7; 3 – 0.9 and 4 – 1.4 W/cm^2($\lambda_{ex} = 514.5$ nm; T = 300 K).

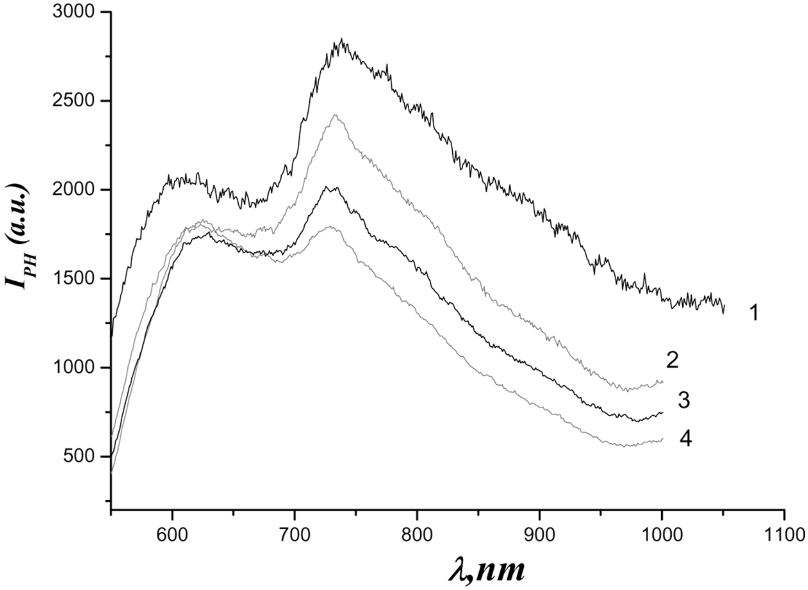

FIGURE 5 PL spectra of PVK + 3 wt% C_{60} for different incident light flux densities (P): 1 – 0.3; 2 – 0.8; 3 – 1.5 and 4 – 1.7 W/cm^2($\lambda_{ex} = 514.5$ nm; T = 300 K).

Figures 4 and 5 show the results of the measurements of the PL spectra of PVK-0.5 wt% C_{60} and PVK-3 wt% C_{60} composites at T = 300 K with different densities of the exciting light flux (P). From the presented figures it can be seen that the luminescence intensity decreases with an increase in P. With the change of P a change in the form of luminescence spectrum occurs too. That indicates that the photo-induced changes in the luminescent centers of the composite or in the channels of the admission to them of excitation. The form of luminescence spectra does not depend on the time of its exhibition (t_e), if the time $t_e > 600$ s. The measurements of the PL spectra of samples to their lighting and after exposure of samples in the darkness during several minutes showed their identity. This follows that the relaxation time of the photo-induced changes in the composites does not exceed several minutes.

The dependence of the properties of the PVK-C_{60} composites on the intensity of the exciting lighting was investigated with the aid of the measurements of its transmission spectrum depending on the intensity of incident light. The results of these measurements are presented in Figure 6. In the spectra for PVK + 3 wt% C_{60} the contribution of the interfering rays, reflected from the boundaries of sample is not

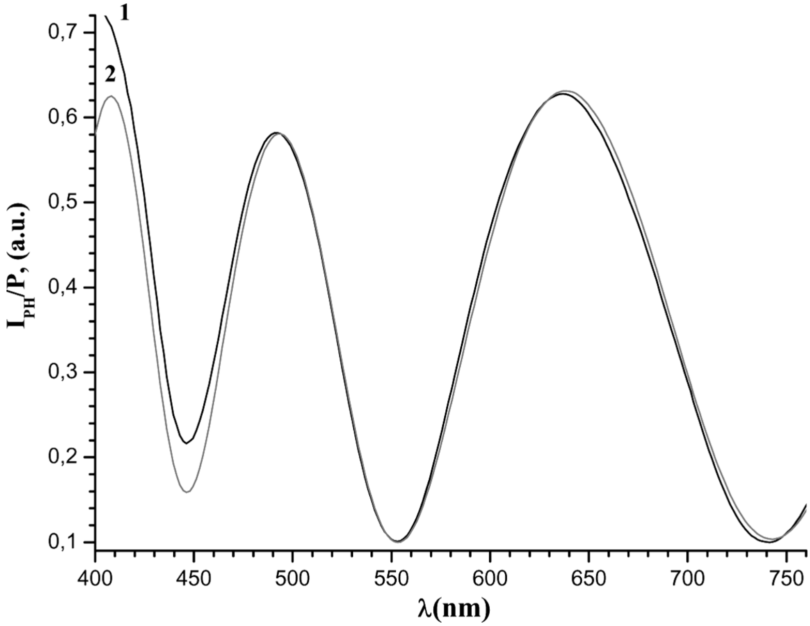

FIGURE 6 Dependence of the intensity of transmitted light (I_P) through the PVK + 3 wt% C_{60}layer at T = 300 K for different incident light flux densities (P): 1 – 0.5 and 2 – 5 W/cm^2.

deducted and that caused to its quasi-periodic form. From these data it is evident that the absorption of the composite increased with the growth of P by a value of 3% that is more than by an order exceeds the accuracy of measurements. Thus, the data, presented in Figure 6 as well as presented in Figures 4 and 5, showed the possibility of existence of the photo-induced structures in the PVK-C_{60}composites, which possess nonlinear optical properties.

CONCLUSIONS

Thus, the data analysis, presented in the Figures, allowed us to give the following conclusions:

1. The luminescence spectrum of the PVK layers, obtained with the aid of the evaporation in the vacuum, essentially differs from the spectra of the samples, prepared both with the aid of watering from the toluene solution and with the use of a procedure of evaporation in an inert gas atmosphere. This property can be explained by the

assumption that in the process of the PVK molecule evaporating their disintegration to the separate fragments occurs, whose nature depends on the properties of the medium, in which the evaporation takes place (its composition, pressure). During the precipitation of the fragment of molecules the repolymerization and packing of the PVC molecules occur, which depend on the properties of fragments and the rate of their coming in. During precipitation the fullerene molecules are condensed in the associates, whose size depends on the C_{60} concentration. On the PVK-C_{60} associate interfaces it is possible that two-dimensional nanostructures such as the quantum wells or superlattices appeared, whose properties depend on a difference in the work functions from PVK and C_{60} associate.

2. The spectral form (position and the half-width of peaks, their quantity) of photoluminescence of PVK-C_{60} composites substantially depends on the concentration of fullerenes, intensity of exciting light and the temperature of sample.
3. The luminescence spectrum of PVK-C_{60}composites cannot be presented (with the error not less than 10%) in the form to the linear combination of PVK and C_{60} spectra both at the room and nitric temperatures. It appears from this that the charge-transfer complex introduces the contribution into the luminescence spectrum of composite.
4. Under the action of light with the wavelength of 514.5 nm the photo-induced reversible changes take place in the PVK-C_{60} composites, which lead to the concentration dependent changes in the PL spectrum.

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