Semiconductor Physics, Quantum Electronics & Optoelectronics, 2022. V. 25, N 1. P. 049-057.

Hetero- and low-dimensional structures

Photoluminescence of melanin-based nanocomposites with fullerene derivative

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Abstract. This paper presents the study of the photoluminescent properties of molecular compositions consisting of melanin and an electron-acceptor material – fullerene derivative, [6,6]-phenyl C61 butyric acid methyl ester (PCBM). These molecular compositions have not been studied well and are promising for molecular electronics of natural materials, in particular, for organic solar cells. The novelty of this work relates to the study of photoluminescence spectra obtained for these molecular compositions and nanocomposites in various solvents (chloroform, acetonitrile, and toluene) as well as in a polystyrene matrix; these studies were carried out at various, in particular, liquid helium (4.2 K), temperatures. The obtained results allowed us to ascertain mechanisms of the state of aggregation and donor-acceptor interaction between melanin and PCBM.

Keywords: photoluminescence, melanin, PCBM, C_{60}, charge transfer state, time-resolved emission spectrum, donor-acceptor complex.

https://doi.org/10.15407/spqeo25.01.049
PACS 78.20.-e, 78.55.Bq, 78.55.Kz, 78.66.-w, 78.66.Tr

Manuscript received 19.11.21; revised version received 25.12.21; accepted for publication 22.03.22;

1. Introduction

1.1. Optical properties of fullerenes

To a first approximation, the UV and visible absorption spectra of fullerenes retain the characteristic features of molecules in the gas phase or solution. In this sense, fullerenes are typical molecular crystals. But decrease in symmetry and the presence of a crystal field in fullerene affects the selection rules and the energies of intermolecular excitations (shift and splitting of degenerate electronic levels). Fullerene optics is equally dependent on both intramolecular and intermolecular electronic processes. The first process leads to the appearance of Frenkel excitons, while the second one is attributed to charge transfer excitons (CT-excitons). The electronic level diagram of C_{60} in the solid and molecular states is given in [1, 2]. Optical transitions between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) zones are forbidden by symmetry. Two lower transitions: ($h_u \rightarrow t_{1u}$) – are forbidden, ($h_u \rightarrow t_{1g}$) – are allowed. Inside the HOMO–LUMO C_{60} band, there are symmetry-forbidden Frenkel excitons and CT-excitons with the energies 1.55, 1.87, 2.2, 2.4 eV [3]. The first allowed exciton has the energy close to 3.6 eV.

1.2. Photoluminescence of PCBM fullerene monomeric molecules and their aggregates

PCBM is a fullerene derivative consisting of a C_{60} molecule with a donor fragment attached to it, the name of which is included in the molecule abbreviation: [6,6]-phenyl C61 butyric acid methyl ester (PCBM) (Fig. 1).

The chemical formula of the PCBM molecule is written as follows: 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6). Due to the presence of a donor tail, PCBM has better solubility than pure C_{60} molecules. The study of fullerene molecules in various solutions provides information on the electronic structure of the molecules, their interaction with the environment, and potential energy transfer in the interaction process. Taking into account the prospects of using fullerene films obtained from solutions, as well as the fact that the photoluminescence (PL) spectra of PCBM in solutions have not been researched comprehensively, we studied absorption and PL spectra of PCBM molecules in polystyrene films and organic solvents (chloroform, toluene, acetonitrile, N-methylpyrrolidone – NMP) of various concentrations. For C_{60} molecules, a weak photoluminescence peak was observed, which is attributed to forbidden $h_u \rightarrow t_{1u}$ transitions [1, 2].

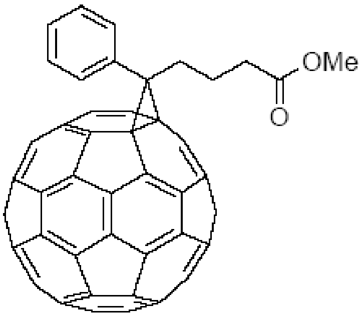

Fig. 1. PCBM molecular structure.

As mentioned above, these transitions turn out to be partially allowed due to the symmetry breaking of the vibrational mode or structural order [2, 4–6]. This peak is stronger in solutions with PCBM. This phenomenon can be explained by the fact that C_{60} molecule transforms into a dipole by the donor polymer fragment. And for molecules with a dipole moment, there is no strictly defined symmetry, *i.e.*, the ground state is neither symmetric nor antisymmetric [4–6]. In other words, we can say that the h_u state goes into the $h_{u,g}$ state. Of course, now the transition is partially allowed, and we can observe it experimentally.

2. Experimental

We studied acetonitrile solutions of natural melanin of plant origin obtained by an extraction [7–10]. PCBM molecules (Sigma-Aldrich) in polystyrene films and organic solvents (chloroform, toluene, acetonitrile, N-methylpyrrolidone – NMP) were studied at various concentrations 10^{-3}, 10^{-4}, and $5\cdot10^{-5}$ wt.% (mass of solute *vs* the total mass of solution). Mixtures of PCBM with melanin in equal mass proportions (1:1; 10^{-3}, $5\cdot10^{-4}$, and $5\cdot10^{-5}$ wt.%) in acetonitrile were studied for fresh mixtures and aged for 24 hours ones, where melanin-PCBM precipitate has formed. The spectral features of the precipitated material have been studied as well. PCBM films on a silica substrate obtained from a toluene solution of PCBM have been studied for comparative analysis. To remove residual toluene, the as-deposited PCBM films were heated to the temperature 200 °C, resulting in the solvation shell of toluene being removed from the fullerene fragments.

PL spectra were studied within the range 650-850 nm at the temperatures 296, 77 and 4.2 K. PL excitation spectra were measured with a Hitachi MPF-4 spectrophotometer. Steady-state and time-resolved PL spectra were recorded with an SPM-2 monochromator equipped with a photoelectric attachment. The spectral slit width was 0.2-0.4 nm. PL was excited using a 337.1-nm pulsed nitrogen laser with the pulse repetition rate 100 Hz, pulse duration 10 ns, and pulse power close to 5 kW [11]. To record the kinetics and time-resolved PL spectra, we used a stroboscopic system with a "time window" of 0.1 ns [11]. The system allowed recording the PL spectra with different nanosecond time delays t_s relatively to the laser pulse. PL was also excited using the pulsed nitrogen laser at the excitation wavelength (λ_{ex}) 337.1 nm. Besides, PL spectra and kinetics of PL were recorded using the LifeSpec II spectrofluorometer with the wavelengths λ_{ex} = 255, 385, 405 nm.

3. Results and discussion

3.1. Absorption and photoluminescence of PCBM in polystyrene

Fig. 2 shows the absorption spectra of PCBM in polystyrene (curve *1*) at 4.2 K. The concentration of PCBM in polystyrene for these measurements was $C = 10^{-4}$ wt.%. In the absorption spectrum of a film prepared from the solid solution of PCBM in polystyrene at 4.2 K, the molecular absorption band of PCBM with the maximum at 695 nm can be distinguished. At the temperature rising from 4.2 up to 296 K, the absorption curve broadens and the band features become less evident. In the absorption spectra of C_{60}, the pronounced band structure is absent, which can be associated with the symmetry-forbidden transition $h_u \rightarrow t_u$ [1]. In the PL spectra, this transition is allowed due to the odd vibrational mode [2–6]. For PCBM, the presence of a donor fragment transforms the molecule into a dipole. For polar molecules, the ground state has no strictly defined symmetry. We can say that the ground state has a mixed (symmetric and antisymmetric) symmetry $h_{u,g}$. For this reason, the transition to the lowest excited state $h_{u,g} \rightarrow t_u$ becomes partially allowed and can be observed in the absorption spectra.

PL of PCBM in polystyrene was studied for the concentrations $C = 10^{-5}$ (Fig. 2) and 10^{-4} wt.% (Fig. 3) at 296 and 4.2 K. For low concentrations (Fig. 2), in the PL spectrum of PCBM at 296 K (curve *3*), a band with a maximum at 705 nm is attributed to monomeric radiation from the t_u state. Due to the temperature decrease down to 4.2 K, this band narrows (Fig. 2, curve *2*), but its position doesn't change.

An increase in PCBM concentration in a polystyrene solution to 10^{-4} wt.% (Fig. 3) leads to non-comventional behavior of the PL spectra, when the temperature changes. At the temperature 296 K, the position

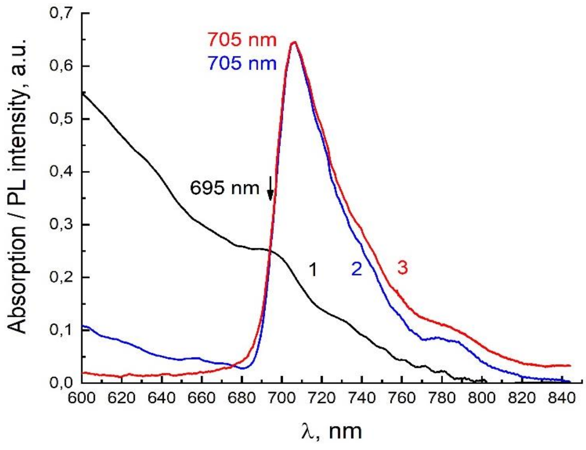

Fig. 2. Spectra of absorption (*1*) and PL (*2*, *3*) for PCBM solid solutions in polystyrene at 4.2 (*1*, *2*) and 296 (*3*) K; λ_{ex} = 337.1 nm; $C = 10^{-4}$ (*1*) and 10^{-5} (*2*, *3*) wt.%.

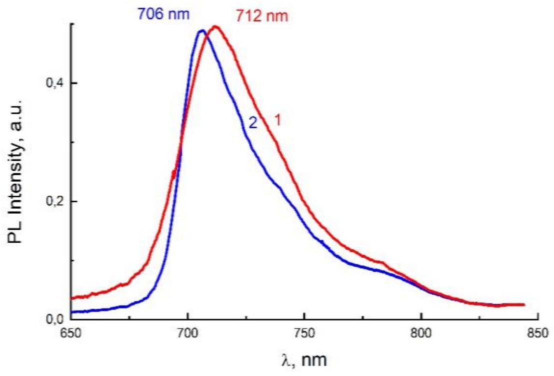

Fig. 3. PL spectra for PCBM solid solutions in polystyrene at 296 (*1*) and 4.2 (*2*) K; λ_{ex} = 337.1 nm; $C = 10^{-4}$ wt.%.

of the PL band maximum (Fig. 3, curve *1*) is observed at 712 nm, and with the temperature decrease to 4.2 K (Fig. 3, curve *2*), the maximum shifts to 706 nm. It can be assumed that the fullerene molecules in the film are arranged irregularly, and some of them are in pre-dimeric states. It leads to the observation of excimer radiation at high temperatures. Lowering the temperature down to 4.2 K leads to dimensional limitations, and formation of excimers practically does not occur. In the PL spectra at low temperatures, monomeric radiation is mainly observed. Excimers have features of optical absorption corresponding to monomers, but observed in the fluorescence spectra are broad structureless bands characteristic for the complexes, such as physical dimers. These are dimers that only exist in an excited state. The ground state of such a pair is unstable.

3.2. Photoluminescence of PCBM solution in chloroform

Fig. 4 shows the PL spectra for PCBM solutions in chloroform. These studies were carried out for the concentrations $C = 10^{-5}$ (*1*, *3*) and 10^{-3} (*2*, *4*) wt.% at 296 (*1*, *2*) and 77 (*3*, *4*) K. For the low concentration ($C = 10^{-5}$ wt.%), a band with a maximum at 702 nm is observed at 296 K (Fig. 4, curve *1*), which can be associated with monomeric radiation from the t_u state. When the temperature decreases down to 77 K, this band (Fig. 4, curve *3*) narrows, but its position does not change significantly. An increase in the PCBM concentration in solution up to 10^{-3} wt.% leads to unconventional behavior of the PL spectra (Fig. 4, curves *2*, *4*). For 296 K, the position of the PL band (Fig. 4, curves *1*, *2*) is the same regardless of concentration, and at 77 K the band shifts to higher wavelengths, and its maximum appears at 720 nm (Fig. 4, curve *4*). This behavior of PL for PCBM solutions at high concentrations can be associated with the processes of molecular aggregation. Taking into account the mentioned above, we conclude that the shift of the PL spectra for solutions of PCBM in chloroform at high concentrations to higher wavelengths with decreasing the temperature is mainly associated with appearance of aggregates of the physical dimer type. The physical dimer consists of two identical molecules located in the space closer to each other than to other molecules, and oriented in a certain way. The molecules in the physical dimer do not form a chemical bond with each other.

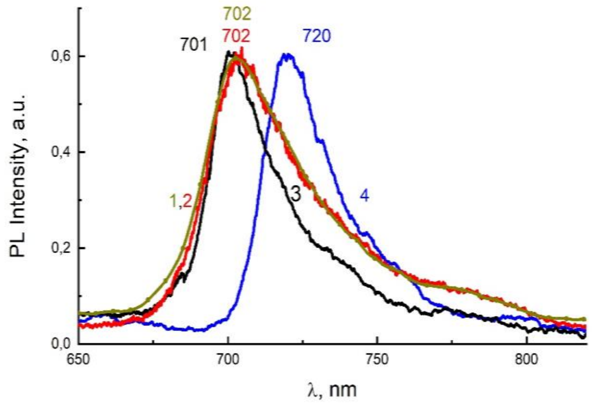

Fig. 4. PL spectra for PCBM solutions in chloroform at 296 (*1*, *2*) and 77 (*3*, *4*) K; λ_{ex} = 337.1 nm; $C = 10^{-5}$ (*1*, *3*) and 10^{-3} (*2*, *4*) wt.%.

The difference in the emission spectra for PCBM molecules in chloroform and polystyrene can be attributed to different interactions of PCBM molecules with the matrix. When the polystyrene films are dried, pores are formed, and the PCBM molecules get into the pores and can be in the pre-dimeric states. At room temperature, PCBM molecules in the pores at optical excitation can get closer to the van der Waals radius and generate excimer irradiation. If the pore diameter is so small that only one PCBM molecule can fit inside, then regardless of temperature, we will observe monomeric radiation.

3.3. Photoluminescence for PCBM molecular solution in various organic solvents

Fig. 5 shows the PL spectra for PCBM molecular solutions in various organic solvents at the low concentration $C = 10^{-5}$ wt.% at 296 K for different excitation wavelengths. Table 1 shows different positions of the PL bands maxima for the PCBM in various organic solvents. It was also found that for a PCBM solution in acetonitrile, the position of PL maximum strongly depends on the wavelength of the exciting light (λ_{ex}). At λ_{ex} = 405 nm, the maximum of the PL band inherent to PCBM in acetonitrile is located at 673 nm, and at λ_{ex} = 255 nm, the PL band of PCBM has its maximum at 690-700 nm.

Table 1. The positions of maxima related to the PL bands (λ_{max}) for the PCBM in various organic solvents at 296 K, $C = 10^{-5}$ wt.%.

Solvent	λ_{ex}, nm	λ_{max}, nm
acetonitrile	405	673
acetonitrile	255	690-700
toluene	405	704-707
NMP	405	711
chloroform	337	702
polystyrene	337	700-709

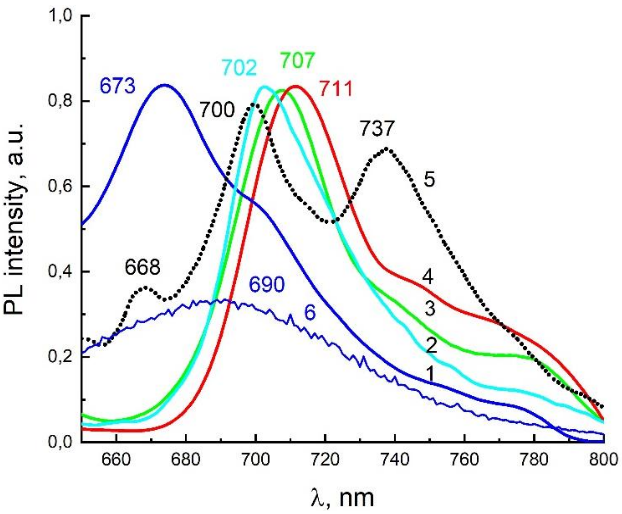

Fig. 5. PL spectra for solutions of PCBM (*1–4*, *6*) and C_{60} (*5*) in acetonitrile (*1*, *6*), chloroform (*2*), toluene (*3*, *5*), NMP (*4*) at 296 (*1–4*, *6*) and 4.2 (*5*) K at λ_{ex} = 255 (*6*), 337.1 (*2*, *5*) and 405 nm (*1*, *3*, *4*); *C* = 10^{-5} wt.%.

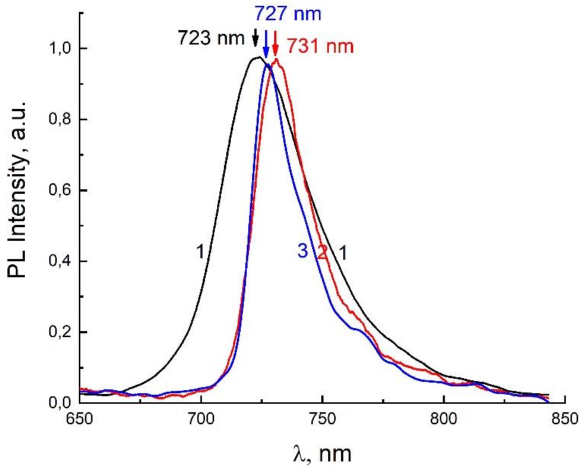

Fig. 6. PL spectra of PCBM films at 296 (*1*), 77 (*2*), and 4.2 (*3*) K; λ_{ex} = 337.1 nm.

Also Fig. 5 shows the PL spectrum of C_{60} in toluene for *C* = 10^{-5} wt.% at 4.2 K (curve *5*). In this spectrum, PL bands appear featuring both molecular (668, 700 nm) and aggregated forms (737-nm band) of C_{60}. From a comparative analysis of the PL spectra inherent to PCBM and C_{60}, it can be concluded that the 673-nm band for PCBM has the same nature as the 668-nm band for C_{60}.

Although the PCBM itself has donor-acceptor properties, depending on the solvent, the molecule can be neutral or polar. For the polar form of PCBM, a charge from the non-fullerene donor fragment can be transferred to the fullerene part. The PL spectrum of the polar form of PCBM can be close to the ionic form of C_{60} and has emission in the region of band peaking at 700 nm [12]. The electronic structure of the neutral form of PCBM is close to that of C_{60}, so the PL band at 673 nm should correspond to this form.

3.4. Photoluminescence of PCBM molecules in a film from a toluene solution

Fig. 6 shows the PL spectra of PCBM films obtained from a toluene solution. As the temperature was lowered from 296 down to 4.2 K, the PL spectra were shifted to longer wavelengths and bands narrowed (Fig. 6). The maxima of PL bands, depending on the temperature (296, 77, and 4.2 K), were at 723, 731, and 727 nm, respectively. For PCBM solutions in toluene, the maximum of PL band is located at 707 nm (Fig. 5, curve *3*). The observed long-wave shift of the maxima of PL bands in PCBM films can be associated with formation of various types of aggregates, structurally similar to physical dimers.

3.5. Photoluminescence of fullerene molecules in melanin

The molecular structure of studied melanin is close to that of synthetic melanin, which is based on the 5,6-indolequinone monomer [13–16]. 5,6-indolequinone molecules are chemically bound with each other and form polymers or planar two-dimensional molecular oligomers [7, 8–10, 17–19] in the form of macromolecular disks, in which chromophores with different lengths π–π conjugation can be distinguished. Furthermore, one-dimensional stacked aggregates (nanoclusters) can be formed from the two-dimensional oligomers.

Fig. 7 shows the PL spectra of acetonitrile solutions of neat melanin (curve *1*) and melanin with PCBM (curves *2–4*) in equal proportions at 296 K (curves *1–3*) and 4.2 K (curve *4*). The PL spectra of the melanin solution at room temperature have a broad band with a maximum located near 470 nm. Due to the weak interaction between stacked melanin oligomers in the ground state, they form pre-dimeric structures. Furthermore, due to weak intermolecular interaction in the ground state, both molecular and excimer (470 nm band – Fig. 7, curve *1*) melanin emission can be observed in the PL spectra of solutions. Depending on the size of oligomers, the

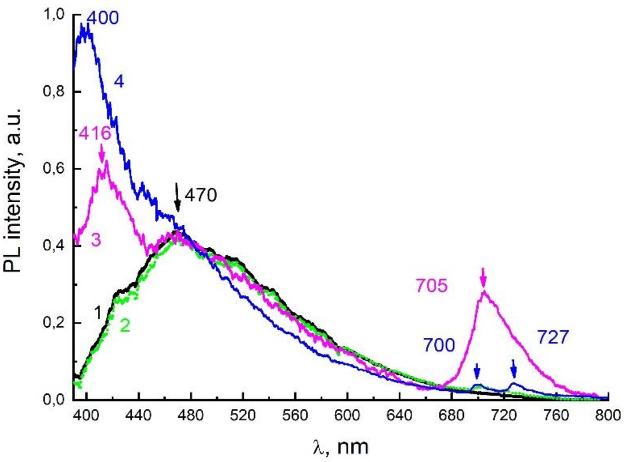

Fig. 7. PL spectra of acetonitrile solutions of neat melanin (*1*) and mixtures of melanin with PCBM at the concentrations $5 \cdot 10^{-5}$ wt.% (*2*, *4*) and $5 \cdot 10^{-4}$ wt.% (*3*) at 296 K (*3*) and 4.2 K (*4*).

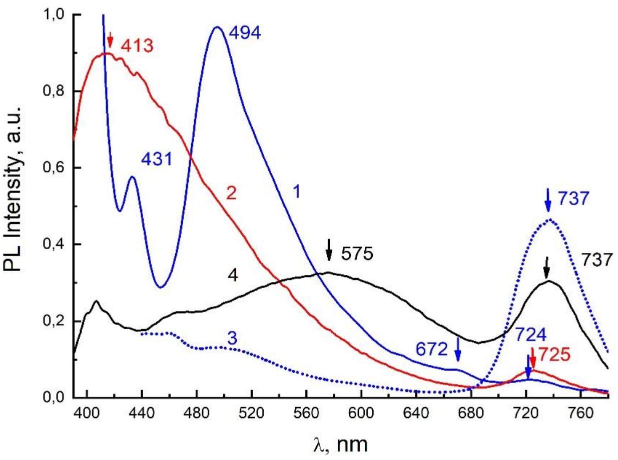

Fig. 8. PL spectra of melanin–PCBM mixtures in acetonitrile with the concentration $C = 5\cdot10^{-5}$ wt% directly after preparation (*1*), and after 24 hours (*2*), precipitate melanin-PCBM (*3*) in acetonitrile for the concentration $C = 10^{-3}$ wt%; melanin–PCBM films formed from precipitate (*4*); $T = 296$ K, $\lambda_{ex} = 385$ (*1*), 337.1 (*2*, *4*), 405 (*3*) nm.

degree of π–π conjugation of monomers in oligomers, and the degree of overlapping of stacked melanin fragments in the excited state, the PL band maximum fluctuate between 460 and 480 nm. Monomer radiation has a shorter lifetime than excimer radiation and is shifted to shorter wavelengths with respect to the eximer peak and dominates in PL spectra at low temperatures. At these temperatures, due to structural obstacles, formation of excimer states between two melanin oligomers is difficult, and in the PL spectra of solutions, monomeric emission of individual chromophores in oligomers is mainly observed. Since melanin consists of indole derivatives, the low-temperature (4.2 K) PL spectra of melanin solutions with the emission band at 400 nm (Fig. 7, curve *4*) can be attributed to monomeric radiation.

When mixing solutions of PCBM and melanin in equal mass proportions, in the PL spectra of the as-prepared solution (Fig. 7, curves *2*–*4*), along with monomeric radiation of melanin, PL of PCBM is observed, both in molecular (bands 700-706 nm) and aggregated forms (band 727 nm). It can be seen from Fig. 7 that at room temperature the molecular radiation of PCBM is observed. The emission band of PCBM molecules in acetonitrile has a maximum near 673 or 690 nm, depending on the excitation wavelength (Table 2). Due to the interaction of PCBM with melanin, these bands disappear, and in the PL spectra, a band at 705 is observed, which can be associated with emission of weak CT complexes of melanin–PCBM. Weak complex formation leads to quenching of the excimer luminescence of melanin, an increase in monomeric radiation and the emergence of a new 416-nm PL band (Fig. 7, curve *3*). For melanin-PCBM solutions cooled to 4.2 K, in the PL spectra, along with molecular radiation of PCBM (band at 700 nm), emission of molecular aggregates of PCBM (band at 725 nm) is observed.

In the mixture of melanin and PCBM in solution, strong interaction of suspended melanin nanoclusters with PCBM molecules occurs. As a result of this interaction, PCBM molecules aggregate on the surface of melanin nanoclusters, the latter become heavier and form precipitates. Fig. 8 shows the dynamics of the changes in the PL spectra, depending on the preparation time and state of aggregation. Curve *1* in Fig. 8 reflects the PL spectra of freshly prepared melanin–PCBM in acetonitrile. In the PL spectra, one can distinguish the emission band of melanin nanoclusters (494 nm) and PL emission for the PCBM (bands at 672 and 725 nm). For the neat solution of PCBM in acetonitrile, PL bands have a maximum at 673 or 690 nm depending on λ_{ex}.

Melanin nanoclusters promote aggregation of PCBM molecules on them and enhance PL due to the transfer of energy from melanin nanoclusters to PCBM. In addition, the differences in PL spectra of PCBM aggregates in organic solvents *versus* melanin can be associated with additional interactions between PCBM and melanin molecules. As can be seen from Fig. 8 (curve *1*), a new band at 431 nm appears in the PL spectrum of the melanin–PCBM mixture solution, which can be associated with formation of donor-acceptor (D–A) complexes between melanin and PCBM molecules. The measurements carried out in 24 hours after preparation of the melanin–PCBM mixture showed that the PL spectra (Fig. 8, curve *2*) changed significantly. A significant drop in the excimer radiation of melanin nanoclusters and an increase of PL in the region of 413 nm are observed. According to our previous studies, for solutions of melanin with the electron acceptor TNF, D–A emission of melanin–TNF complexes was observed in this spectral region [7]. Therefore, it can be also assumed that for melanin–PCBM solutions, the D–A emission of melanin–PCBM complexes is observed. In the long-wave region of the PL spectrum of melanin–PCBM solutions, a decrease in the intensity of 672-nm band, and an increase in the 725-nm band are observed, which indicates a further increase in aggregation of PCBM molecules.

An increase in the concentration of PCBM up to $C = 10^{-3}$ wt.% in these mixtures leads to precipitation of molecular complexes of melanin–PCBM, formed as a result of aggregation of PCBM molecules on the surface of melanin nanoclusters and an increase in their mass. Fig. 8 (curve *3*) shows the PL spectra of solutions (precipitate) of melanin–PCBM in acetonitrile with an increase in PCBM concentration up to 10^{-3} wt.%. In the PL spectrum of the melanin–PCBM precipitate in acetonitrile, there is a significant increase in the intensity of the band (737 nm) associated with the emission of PCBM nanoaggregates on the surface of melanin nanoclusters. With formation of the crystalline PCBM nanoaggregates on the surface of melanin nanoclusters, a significant growth of the PL band peaking at 737 nm and quenching of the melanin PL in the short-wave region are observed. The results can be explained by the presence of photoinduced transfer of the melanin exciton energy to

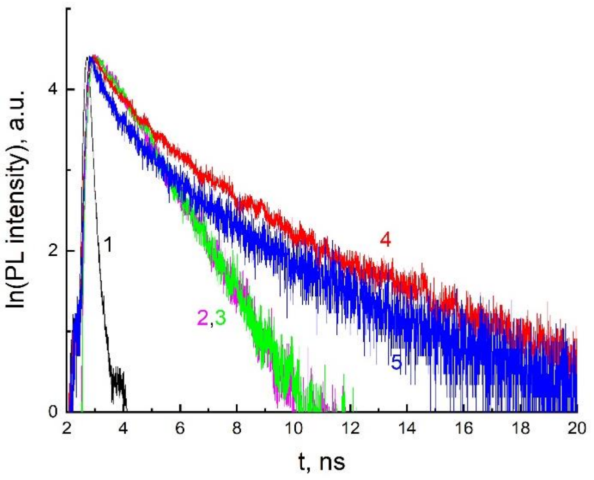

Fig. 9. PL kinetics of acetonitrile solutions of the melanin–PCBM precipitate (*2*–*4*) and neat melanin (*5*) at 296 K for various radiation wavelengths – 500 (*4*, *5*), 720 (*2*) and 750 nm (*3*). The Instrument Response Function (*1*); λ_{ex} = 405 nm.

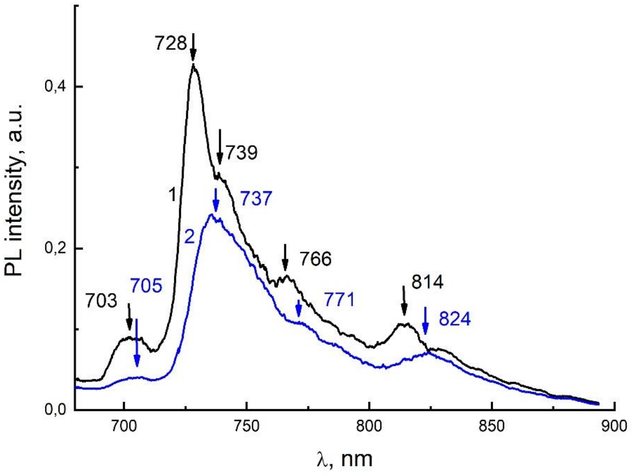

Fig. 10. PL spectra of the melanin–PCBM film (*1*) and the precipitate in melanin–PCBM in acetonitrile solution (*2*) at 4.2 K, λ_{ex} = 337.1 nm.

the adsorbed PCBM molecules. The process of fullerene sensitization by charge transfer between it and its environment was observed earlier [20]. The high efficiency of electron trapping by a fullerene molecule is also defined by the fact that fullerene is an effective oxidant (acceptor).

Our results show that this process is efficient near the surface of melanin nanoclusters and PCBM. Fig. 8 (curve *4*) shows also the PL spectra of the film obtained from the melanin-PCBM precipitate in acetonitrile when heating up to 200 °C. In addition to the 737-nm band, a broad structureless band with a maximum at 575 nm is observed in the PL spectra of the melanin–PCBM film.

Fig. 9 shows the PL kinetics of solutions (precipitate) of the composite for melanin–PCBM (*2*–*4*) and melanin (*5*) in acetonitrile at 296 K for different radiation wavelengths. For the melanin–PCBM composite (precipitate), the PL kinetics was measured in the emission regions of melanin (500 nm) and PCBM (720 and 750 nm). In addition, the PL kinetics of melanin in acetonitrile (500 nm) was measured. The PL kinetic curves are well described by a one- or three-exponential function:

$$I_{PL}(t) = A_1 e_1^{-t/\tau} + A_2 e_2^{-t/\tau} + A_3 e_3^{-t/\tau}$$

with PL lifetimes within the picosecond and nanosecond ranges. Table 2 shows the calculated PL lifetimes for solutions of melanin–PCBM (precipitate) and melanin in acetonitrile. The kinetics of PL decay in the region of melanin contains fast and slow radiation components. It has been assumed [10, 13] that the fast PL component is associated with the monomeric radiation of melanin nanoclusters, and the slow one is associated with the excimer radiation of these nanoclusters. Aggregation of PCBM molecules on the surface of melanin nanoaggregates leads to quenching of the excimer PL of melanin and a decrease in the lifetime of the excimer radiation. For neat melanin, the slow component of radiation (λ_{PL} = 500 nm) is 4517 ps, and after interaction with PCBM, this component of time decreases down to 4013 ps (Table 2).

The PL lifetimes of neat PCBM molecules ($C = 5\cdot 10^{-5}$ wt.%, λ_{ex} = 405 nm) in various organic solvents have been evaluated. The lifetime values are 1170 ps (λ_{PL} = 670 nm) in acetonitrile, 1607 ps (λ_{PL} = 700 nm) in toluene and 149 ps (λ_{PL} = 700 nm) in solid matrix of polystyrene.

Fig. 10 shows the low-temperature (4.2 K) PL spectra of the melanin–PCBM precipitate in acetonitrile (curve *2*) and the melanin–PCBM film (*1*) obtained from

Table 2. PL lifetimes of melanin–PCBM solutions (precipitates) and melanin in acetonitrile at 296 K for different PL radiation wavelengths. λ_{ex} = 405 nm.

	λ_{PL}, nm	τ_1, ps	%	τ_2, ps	%	τ_3, ps	%	χ^2
melanin–PCBM	500	145	4	1066	18	4013	78	1.100
	720	1550						1.020
	750	1489						1.022
melanin	500	124	8	1057	25	4517	67	1.065

this precipitate. The measured low-temperature spectra are structured and, in many respects, similar to the PL spectra of C_{60} nanoclusters. The PL spectra have an intense emission from crystalline clusters of the PCBM as well. It is much more intense than the radiation from neat PCBM films. The band maximum of this radiation at 296 K is located near 737 nm (Fig. 8). It can be assumed that the intense PL of fullerene moiety at room temperature is largely caused by the efficient transfer of energy from melanin to PCBM molecules. With a decrease in temperature down to 4.2 K, the position of PL maximum inherent to fullerene moiety can change and shift to the short-wave side depending on the delay time during measurements. These changes are more clearly pronounced in the low-temperature PL spectra of the melanin–PCBM systems (Fig. 7). The observed structuring of the PL peaks of fullerene nanoclusters at low temperatures and their shift to shorter wavelengths can be associated with the spectral manifestation of the size quantization effect. As shown in [12], formation of nanocrystallites that are monodisperse in size can lead to a quantum-size effect in optical spectra. To understand the behavior of melanin PCBM aggregation as well as potential aggregation of PCBM itself, the low-temperature PL spectra of C_{60} at various concentrations have been studied.

3.6. Low-temperature PL spectra of C_{60}

Fig. 11 shows the low-temperature (T = 4.2 K) PL spectra of solutions of C_{60} in toluene for the different fullerene concentrations $5 \cdot 10^{-5}$ wt.% (curve *1*) and 10^{-3} wt.% (curve *2*). The PL spectra are a superposition of the emission of molecular (bands at 668 and 700 nm) and aggregated (737, 748 and 820 nm) forms of C_{60}. With an increase in the concentration of C_{60} in solution, the PL intensity of the molecular luminescence decreases, while the emission of nanoaggregated forms of C_{60} increases. With an increase in the concentration of C_{60}, the PL spectrum also shifts to higher wavelengths. It indicates that with an increase in the concentration of C_{60} molecules in toluene, the nanoaggregates in a suspended state grow in their sizes.

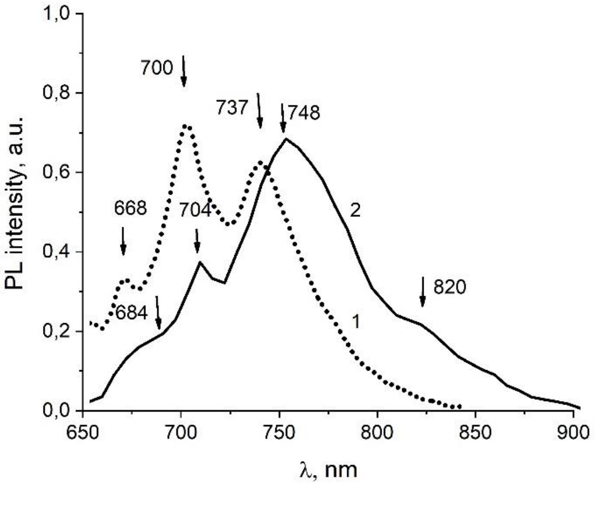

Fig. 11. Low-temperature PL spectra of C_{60} in toluene for the various concentrations: $5 \cdot 10^{-5}$ wt.% (*1*) and 10^{-3} wt.% (*2*), λ_{ex} = 337.1 nm, T = 4.2 K.

In the emission spectrum (Fig. 11, curve *2*) of fullerene nanoaggregates, an intense band at 748 nm and its less intense vibronic iteration at 820 nm can be distinguished. The PL spectra of fullerene film deposited on the silica substrate after evaporation of toluene had a similar shape to low-temperature PL spectra of C_{60} in toluene at 10^{-3} wt.% (Fig. 11, curve *2*). The PL lifetime of the studied fullerene film at 4.2 K is 1.7 ns featuring the lifetime of nanoaggregarted form of C_{60}. Currently, there are several explanations on PL origin for fullerene in the condensed state. It is assumed that PL is related with defects (grain boundary surfaces), leading to local symmetry distortion of the fullerene molecule and an increase in the probability of the radiative $t_{1u} - h_u$ transition, which is forbidden by parity in the dipole approximation [21]. According to [22], PL arises due to localization of electronic excitations (exciton-polaron complexes) on the quasi-two-dimensional spherical fullerene surface. Alternatively, one can give preference to the mechanism of radiative recombination through self-trapped Frenkel excitons on the C_{60} cluster. The possibility of localization can be provided by the presence of relatively weak π-bonds included in the composition of double bonds between carbon atoms. On the short-wave side of the 743-nm band, the bands at 704 and 684 nm can be distinguished. Emission in this region is due to local structural imperfections in the environment of C_{60} molecules, and as a result of the distortion of molecular orbitals affecting the electronic states of C_{60} molecules (X-trap states) [22]. Additionally, our data indicate that excitons with charge transfer localized on neighboring molecules can also be excited at the sites of defects in C_{60} nanocrystals [23].

4. Conclusions

The PL spectra of PCBM dissolved in chloroform, toluene, and polystyrene at the temperatures 4.2, 77 and 296 K have been studied. Depending on the solvent and the wavelength of the exciting light, PL bands are observed with the maxima at 670 and 705 nm. Although these transitions are forbidden in the C_{60} molecule, for PCBM, due to symmetry breaking, they become partially allowed. The observed PL band at 670 nm can be associated with the neutral form of the PCBM, and the 705-nm band is attributed to the ionic form of molecule.

As a result of our studies, the possibility to change PL properties of melanin nanoclusters due to the physical and chemical adsorption of PCBM molecules on their surface has been shown. The effect of PL intensity amplification in PCBM due to their interaction with melanin has been found. The effect is caused by the photoinduced transfer of excitation energy from melanin to PCBM molecules adsorbed on the surface of melanin nanoclusters, is followed by radiative recombination in PCBM. The possibility of sensitizing PL of PCBM molecules by melanin has been shown.

The experimental data on the PL spectra for solutions of the natural melanin with an electron acceptor PCBM in acetonitrile indicate formation of weak CT-complexes between melanin and PCBM molecules. In particular, the nature of the 705-nm band in solutions of melanin with PCBM can be associated with formation of CT complexes between melanin and PCBM molecules. Furthermore, the emergence of intense PL 400-430 nm bands in two-component systems of melanin with PCBM and the quenching of the excimer melanin band at 460-480 nm can be associated with formation of weak CT-complexes between monomeric constituents of the melanin oligomer and PCBM.

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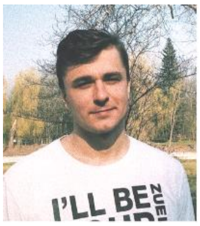

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Фотолюмінесценція нанокомпозитів на основі меланіну та похідного фулерену

А.О. Костецький, Ю.П. Пирятинський, А.Б. Вербицький, П.М. Луцик, А.Г. Рожин

Анотація. У цій роботі представлено дослідження фотолюмінесцентних властивостей молекулярних композитів, що складаються з меланіну та електронно-акцепторного матеріалу – похідного фулерену, метилового ефіру [6,6]-феніл-С61-масляної кислоти (PCBM). Такі молекулярні композити недостатньо вивчені і є перспективними для молекулярної електроніки природних матеріалів, зокрема для органічних сонячних елементів. Новизна даної роботи полягає у дослідженні спектрів фотолюмінесценції цих молекулярних сумішей і нанокомпозитів у різних розчинниках (хлороформі, ацетонітрилі, толуолі), а також у полістирольній матриці. Ці дослідження проводилися при різних температурах, зокрема при температурі рідкого гелію (4,2 K). Отримані результати дозволили детальніше розглянути механізми агрегації та донорно-акцепторної взаємодії меланіну та PCBM.

Ключові слова: фотолюмінесценція, меланін, стан перенесення заряду, PCBM, C_{60}, спектр випромінювання з часовим розділенням, донорно-акцепторний комплекс.