Galyna Puchkovska International School-Seminar
Spectroscopy of Molecules and Crystals
XXV
Kyiv, Ukraine 21-24.09.2021

PHOTOLUMINESCENCE OF MELANINE-BASED NANOCOMPOSITES WITH FULLERENE DERIVATIVES

A. O. Kostetskyi[a], *Yu. P. Piryatinski*[a], *A. B. Verbitsky*[a], *P. M. Lutsyk*[b] *& A. G. Rozhin*[b]

(a) Institute of Physics of NAS of Ukraine, Kyiv, Ukraine; (b) Aston University, Birmingham, UK

Corresponding author: **antonkostetskyi@gmail.com*

Introduction:

This work presents the study of the photoluminescent properties of molecular structures based on melanin and an electron-acceptor material - a fullerene derivative, PCBM ([6,6] -phenyl C61 butyric acid methyl ester). Such molecular structures have not been widely studied and are promising for molecular electronics of natural materials, in particular, for organic solar cells. The novelty of this work lies in the fact that photoluminescence spectra were obtained for these little studied molecular structures and composites in various solvents (chloroform, acetonitrile, toluene) and in a polystyrene matrix; these studies were carried out at different, in particular, helium, temperatures. Based on these measurements, were drawn conclusions about the state of aggregation and donor-acceptor interaction between melanin and PCBM.

Materials and methods

We studied aqueous solutions of natural melanin of plant origin obtained by an extraction[1-3]. To record the kinetics and time resolved PL spectra, we used a stroboscopic system with a “time window” of 0.1 ns. It made it possible to record PL spectra with different nanosecond time delays t_s relative to the laser pulse. The PL was excited by a pulsed nitrogen laser at a wavelength of 337.1 nm. The PL spectra were studied at temperatures of 294, 77, and 4.2 K.

Results

Photoluminescence of PCBM molecular solution in various organic solvents

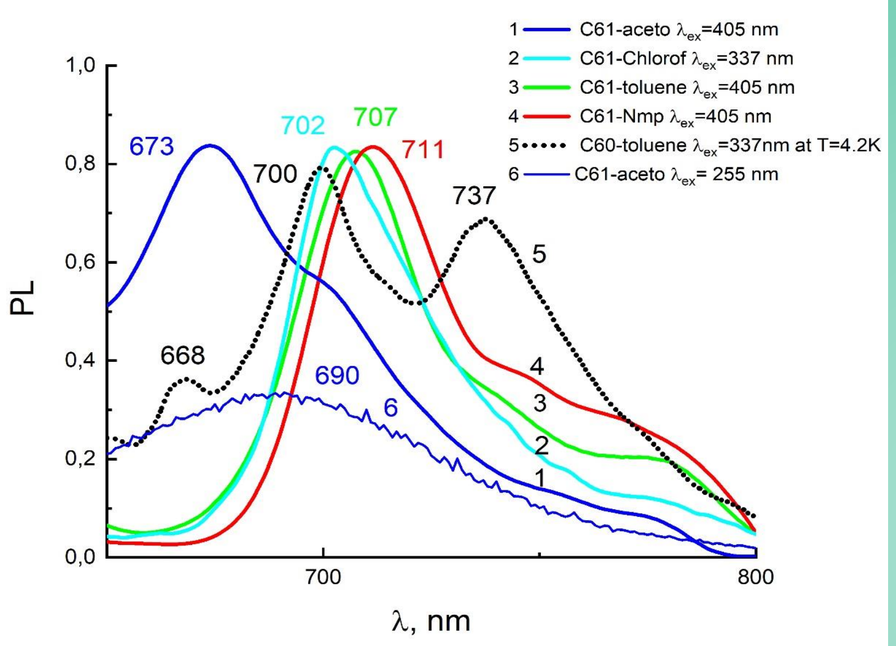

Fig. 1. PL spectra of solutions of PCBM (1-4,6) and C60 (5) in acetonitrile (1,6), chloroform (2), toluene (3,5), Nmp (4) at 296 (1-4,6) and 4.2K (5) at λ_{ex} = 255 (6), 337.1 (2,5) and 405 (1,3,4) nm; C = 10^{-5} wt%

Fig. 1 shows the PL spectra of PCBM molecular solutions in various organic solvents for low concentrations C = 10^{-5} wt% at 296K for different exciting light wavelengths. Although the fact that the PCBM molecule itself has donor-acceptor properties, it can be neutral or polar, depending on the solvent. For the polar form of PCBM, the charge from the donor fragment can be transferred to the fullerene. In the case when the PCBM molecule is neutral, its electronic structure is close to C60, and in this case the PL band at 673 nm will correspond. For the polar form of PCBM, the PL spectrum can be close to the ionic form of C60 and emission in the region of the 700 nm band [4].

Photoluminescence of fullerene molecules in melanin

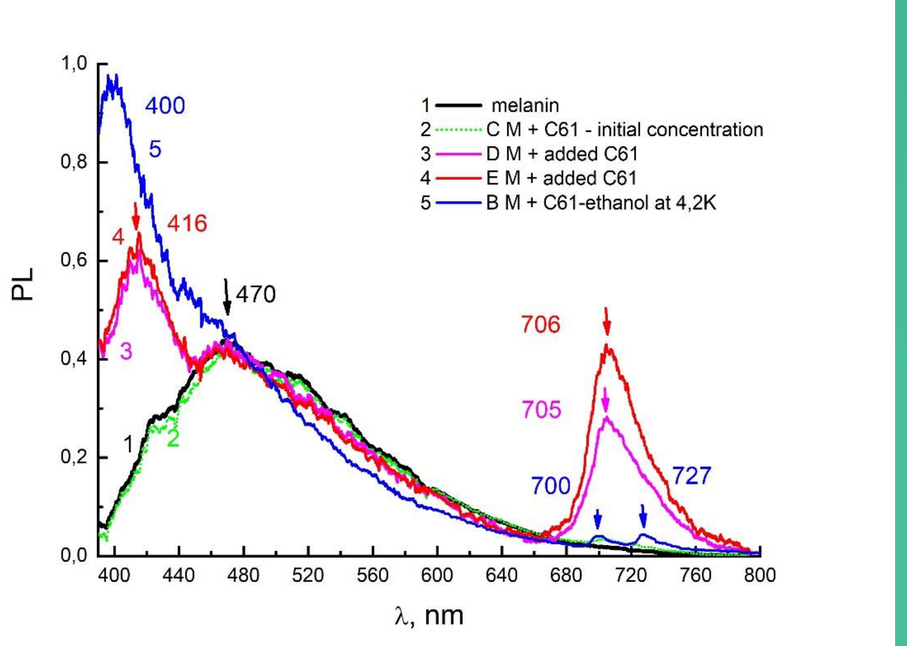

Fig.2. PL spectra of acetonitrile solutions of pure melanin (curve 1) and melanin with PCBM in equal concentrations (curves 2-5) at 296 (curves 1-4) and 4.2 (curve 5) K; C = 5*10^{-5} wt%.

Figure 2 shows the PL spectra of acetonitrile solutions of pure melanin (curve 1) and melanin with PCBM (curves 2-5) in equal proportions at 296 K (curves 1-4) and 4.2 (curve 5) K.

When mixing solutions of PCBM and melanin in equal proportions in the PL spectra of a new solution (Fig. 7, curves 2-5), along with monomeric radiation of melanin, radiation of PCBM is observed, both in molecular (bands 700-706 nm) and in aggregated form (band 727 nm). It can be seen from Fig. 2 that for these concentrations of PCBM in melanin at room temperature, bands are observed, in their spectral position close to the molecular radiation of PCBM. The emission band of PCBM molecules in acetonitrile has a maximum at about 673 or 690 nm, depending on the wavelength of the exciting light. When PCBM interacts with melanin, these bands disappear, and bands at 705 and 706 nm are observed in the PL spectra, which can be considered associated with the emission of weak melanin - PCBM complexes. The formation of weak complexes leads to quenching of the excimer luminescence of melanin, an increase in monomer radiation and the appearance of a new 416 nm band in the radiation (Fig. 7, curves 2-4). When melanin-PCBM solutions are cooled to 4.2 K, in the PL spectra, along with the molecular radiation of PCBM (band at 700 nm), emission of molecular aggregates of PCBM (band at 725 nm) is observed.

Melanin nanoclusters promote aggregation of PCBM molecules on them and enhance PL due to the transfer of energy from melanin aggregates to PCBM aggregates.

For melanin-PCBM solutions, we observe the D-A emission of melanin-PCBM complexes.

An increase in the concentration of PCBM to 10^{-3} wt% in solution leads to the 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. With the formation of crystalline PCBM nanoaggregates on the surface of melanin nanoclusters, a significant increase in the PCBM photoluminescence in the 737 nm region and quenching of the melanin PL from the short-wavelength side of it are observed.

Conclusions:

In the spectral region 650–850 nm, the photoluminescence spectra of PCBM dissolved in chloroform, toluene, and polystyrene at temperatures of 4.2, 77 and 300K are studied.

The effect of increasing in the PL intensity of PCBM upon their interaction with melanin was found. The effect is caused by photoinduced transfer of excitation energy from melanin to PCBM molecules adsorbed on the surface of melanin nanoclusters, followed by radiative recombination in them. The possibility of sensitizing the photoluminescence of PCBM molecules by melanin has been shown.

The experimental data on the PL spectra for solutions of the natural pigment melanin with an electron acceptor PCBM in acetonitrile indicate the formation of weak CT complexes between melanin and PCBM molecules. The appearance of intense PL 400-430 nm bands in two-component systems of melanin with PCBM and quenching of the excimer melanin band at 460-480 nm can be associated with the formation of weak CTs between one of the monomeric constituents of the melanin oligomer and PCBM. The nature of the 570 nm bands in solid solutions of melanin with PCBM can be associated with the formation of CT complexes between melanin and PCBM molecules.

References

[1] Kostetskyi A. O., Piryatinski Yu. P., Verbitsky A. B., Lutsyk P. M. Rozhin A. G. (2018). *Mol. Cryst. Liq. Cryst.*, 671:1, 41-54.

[2] A.O. Kostetskyi, Yu.P. Piryatinski, A.B. Verbitsky, P.M. Lutsyk, A.Rozhin, Time-resolved photoluminescence study of excited states in nanostructured melanin, Molecular Crystals and Liquid Crystals, (2020) v. 697, N 1, pp.31-48.

[3] A. O. Kostetskyi, Yu. P. Piryatinski, A. B. Verbitsky, P. M. Lutsyk & A. G. Rozhin (2021): Dynamics of electron transfer in melanin-trinitrofluorenone system, Molecular Crystals and Liquid Crystals, DOI: 10.1080/15421406.2020.1861522

[4] Боженов А.В., Горбунов А.В. Кинетика фотоиндуцированного поглощения 1.2 эВ в пленках C_{60} // ФТТ.-1996,- 30, №.5,-С.1616-1620

[5] Rosei M.,Moska L., Galuzzi F. Synthetic Metals 1996, v.76, P. 331-335