

# TECHNOLOGY AND SOME OPTICAL PROPERTIES OF NANOCOMPOSITES PEPC/CuPc

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(Received July 19, 2013)

## Abstract

A new structural nanocomposite (NC) based on oligomer poly(N-epoxypropyl)carbazole (PEPC) and copper phthalocyanine (CuPc) nanocrystals on a glass substrate are prepared by casting and droplet methods under normal conditions (room temperature, atmospheric pressure). Thin films of the PEPC/CuPc nanocomposite are characterized by visible optical, infrared (FT-IR), and photoluminescence (PL) spectra. The observed FT-IR bands are assigned to vibration modes of molecules and nanocrystals of CuPc on the basis of their symmetry. The optical spectra of PEPC/CuPc nanocomposites films show three main absorption bands attributed to CuPc, one band positioned at 1.46 eV, another one located at 2.02 eV, which is known as the  $\pi \rightarrow \pi^*$  transitions in Q-bands and the  $\pi \rightarrow \pi^*$  transitions of Soret B-band which was located at 3.02 eV. The effect of irradiation with ultraviolet (UV) light on the optical properties is studied.

## 1. Introduction

Organic compounds of metal phthalocyanine present of special interest because they have strong absorption in the ultraviolet and visible regions and are promising due to their double bond conjugated cyclic [1]. These materials exhibit many interesting properties, e.g., organic semiconductors [2-3], photoconductors [4], electrophotographic materials [5], optical recording media [6-7], and nonlinear optical materials [8] are chemically and thermally stable [9], show catalytic activity [10-11], etc. They also have a potential for application in optical logic devices [12-13], solar cells [14-15], and sensors [15]. Phthalocyanines (PC) belong to a well-studied class of molecules that have a number of wide-ranging applications as diverse dyes [16], light emitting diodes [17], and field-effect transistors, etc. They exist as a range of derivatives, where the polyaromatic ring for the phthalocyanato anion  $C_{32}H_{16}N_{8}$  is most commonly bound to a transition metal (MePc) or hydrogen ( $H_2Pc$ ) [18]. Metal phthalocyanines are well known dye pigments having similarity in structure with biological molecules chlorophyll and hemoglobin. Among the metal substituted phthalocyanine, copper II phthalocyanine was found to have superior properties [19-21].

High vacuum evaporation has become the most widely used technique for the deposition of CuPc films [22]. CuPc has a lower mobility of about  $10^{-4} \text{ cm}^2/\text{V s}$  compared to the conjugated oligomers such as PEPC with a mobility of approximately  $10^{-2} \text{ cm}^2/\text{V s}$ . However, recently, it has

been reported that high mobility of CuPc thin films could be achieved by employing an elevated substrate heating temperature, which directly affects the crystal structure and morphology of the thin layers. These studies have indicated that the orientation of the grains depends on the substrates, the deposition technique, and the heat treatment temperature.

Nanocomposites based on polymers and organic compounds are excellent structures for new devices with modern performance and are good for use in various fields of optoelectronics, technology, medicine, etc. The advantages of NC are the preservation of the physical properties of the polymer and embedded in the matrix material and the appearance of new properties due to the interaction between them, a simple production technology of thin films on various surfaces, etc. Other advantages are high stability of given nanocomposite, attachment and protection of organic compounds and their properties in the polymer matrix. They can be obtained in the form of thin films with on large substrates and in the form of flexible fiber or planar waveguides. Polymers are interesting and promising materials due to their sensitivity to light. Combining the photoconductivity properties and molecular structure will provide the recording of optical information with high resolution. From this point of view, polymers containing the carbazole group—poly(N-vinyl) carbazole or oligomeric poly(N-epoxypropyl) carbazole—are of particular interest. They possess some important properties, such as optical transparency, film forming ability, flexibility, and thermoplasticity and provide high technology at low cost. These polymers are p-type conductivity and are useful for recording of electrophotographic and holographic media [23–24].

Embedding of CuPc in PEPC makes it possible to prepare promising composite materials with photosensitive properties. The paper presents the results of nanocomposite technology, optical and photoluminescence (PL) characterizations of PEPC/CuPc, where PEPC is used as a polymer matrix and CuPc is added at various weight concentrations (0.2, 1, 5, 9, 12, 18%) in the nanocomposites.

## **2. Technology of CuPc and PEPC/CuPc composites and experimental methods**

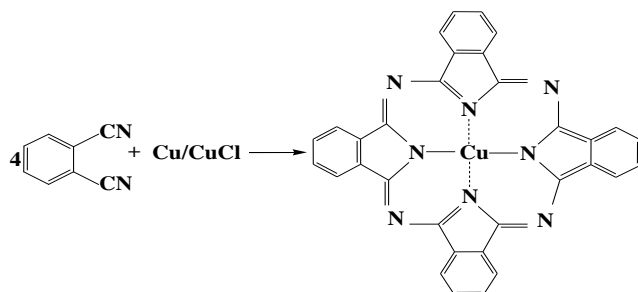
An organic compound of copper phthalocyanine was obtained by a technology similar to that described in [25]. For the synthesis of phthalocyanine, 85 ml of nitrobenzene was admixed with 13.9 g (109 mmol) of 0-ftalonitrile, 1.00 (15.7 mmol) of copper powder, 0.95 g (9.6 mmol) chloride is copper(I), and 40 mg (0.28 mmol) of molybdenum oxide (VI). The active ingredients of the passage ammonia were stirred and heated at 300°C for 2 h and kept at this temperature for 4–5 h.

The precipitate was cooled to a temperature of 80–85°C, filtered through glass filter, and washed several times (the total volume of the solvent was 30 ml) with nitrobenzene heated at 80–90°C. The filter was cleaned in methanol (3 x 50 ml) and twice with water (50 ml) (stirring and filtration). The resulting powder was dried in vacuum to form 13.3 g (91%) of CuPc in the shape of blue-purple fine needles (insoluble in most solvents except in hot charge-three nitrobenzene and partially soluble in DMSO) [25].

PEPC was purchased from Sigma Aldrich Chemical Co. Toluene was used as a solvent for PEPC; the solutions were had densities of up to 100 mg/ml. PEPC films on glass substrate were fabricated by the casting method under normal conditions (room temperature, atmospheric pressure) and then dried at 40°C for 4 h.

Copper phthalocyanine layers were deposited on PEPC thin films by the thermal evaporation method under high vacuum conditions ( $2 \cdot 10^{-4}$  Pa). The CuPc source contained in a tantalum boat was resistively heated. The CuPc powder was used after repeated degassing of the

source prior to deposition. The substrates were located at different distances from the evaporation source to get different layer thicknesses and kept at room temperature. Deposition was observed to occur when current through the boat was kept constant at 20 A. The thicknesses of the deposited CuPc films were calculated preliminarily to obtain some mass amounts of CuPc necessary for the further formation of NCs.

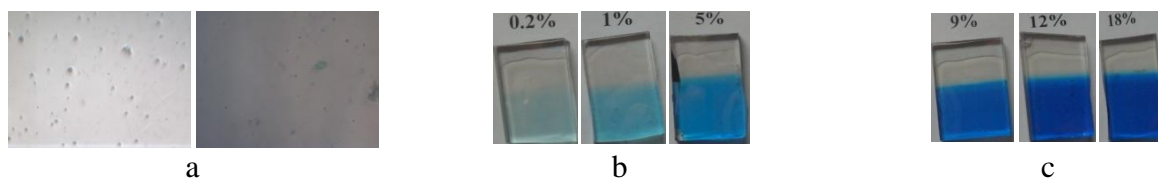


**Fig. 1.** Scheme for obtaining of copper phthalocyanine with symmetry of  $D_{4h}$ .

After deposition of the layers in vacuum, they were annealed at 60 °C for 24 h to establish a homogeneous distribution of copper phthalocyanine material in volume of PEPC to form the composition. In this way, by the method of sublimation and subsequent thermal treatment, copper phthalocyanine was incorporated into PEPC oligomer matrix. This method was used to obtain composites with different concentrations of CuPc sample (0.2, 1, 5, 9, 12, 18%). The NC layer thickness was approximately 1  $\mu\text{m}$ ; the samples were of blue color; the sample surface was smooth, plain, and transparent under a MII-4 microscope (Fig. 2c). According to this, it was concluded that the particle sizes in the polymeric matrix are smaller than 0.1  $\mu\text{m}$  and uniformly distributed over the surface and in the volume of the PEPC oligomer and thus can be considered as nanocomposites.

Measurements of transmission spectra (T) of nanocomposites PEPC/CuPc were performed using a SPECORD-VIS spectrophotometer (Carl Zeiss Jena) (in the spectral range 300–800 nm) connected to computer and a PerkinElmer spectrophotometer (650 to 6000  $\text{cm}^{-1}$ ). PL was measured using MDR-23 (and MDR-24); PL excitation was performed by a nitrogen laser ( $\lambda = 337.1$  nm) with the intensity of radiation in the area ( $P = (0.1 - 10^3)$   $\text{W}/\text{cm}^2$ ,  $\tau_i = 8$  ns) or a laser diode ( $\lambda = 405$  nm) at room temperature.

The morphologic properties of the nanocomposites were investigated using a Linnik MII-4 interferometer and a MIK-4 microscope.



**Fig. 2.** Images of thin films of the PEPC/CuPc nanocomposite samples obtained through transparency (a) x 3.7T transparency and reflection (b) x 40R) on a MIK-4 microscope and (c) photos of the samples.

### 3. Experimental results

#### 3.1. Transmission and absorbance of NC PEPC/CuPc

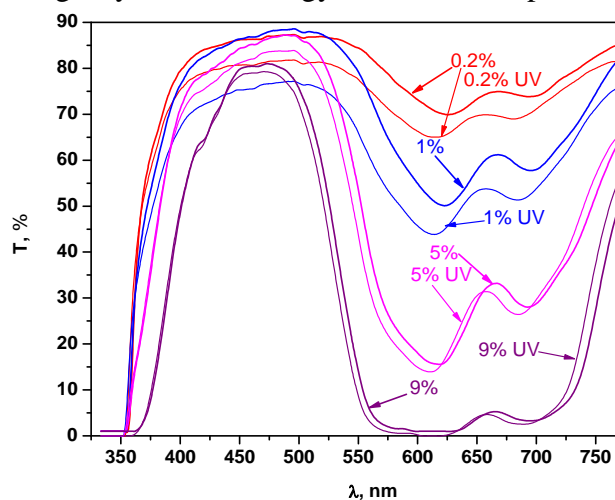
Figure 3 represents the optical transmission spectra of NC PEPC/CuPc thin films. The threshold of the transmission in the UV domain (350–420) nm and two features of transmission in the red (630–750) nm, the intensities of which depend on the concentration of CuPc in nanocomposite, are observed. In the wavelengths greater than 790 nm, the layers are translucent. The increasing concentration of CuPc in the PEPC composite leads to a decrease in the transmission spectrum in this area until completely absorption. The samples of PEPC/CuPc nanocomposites were treated with UV light in a spectrum range of 200–300 nm (Fig. 3) for 1 h. As a result, the transmission of the nanocomposites darkens and their spectra are shifted to UV in all cases of CuPc in NC.

The absorption of NCs is represented in Fig. 4. The absorption coefficient was determined from transmission spectra (Fig. 3) by the formula  $\alpha = -\ln T/d$ , where  $d$  is the thickness of the NC films. In an energy range of 1.25–3.30 eV, we can observe that the absorption spectrum consists of three main maximums and an abrupt threshold, which is typical for metal-phthalocyanine layers in this domain.

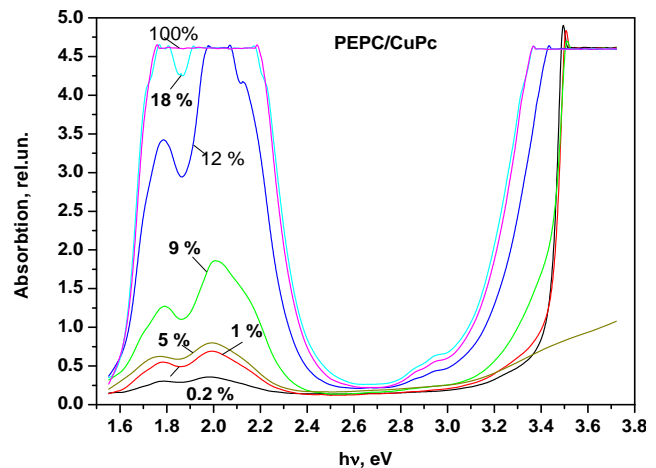
In the  $\alpha(h\nu)$  dependence in the UV part, the absorption threshold is identified to characterize nanocomposites. With increasing concentration of CuPc in NCs, the feature of the absorption line varies only slightly. The maximums of the  $\alpha(h\nu)$  spectra increase with increasing concentration and are attributed to CuPc in NCs.

For calculation of the energies of these bands, the energy dependence of absorption coefficient was analyzed using the formula  $\alpha = \alpha_0(h\nu - E_i)^n$ , where  $E_i$  is the optical band. The dependence of absorption in coordinates  $\lg(\alpha \cdot h\nu) - \lg(h\nu)$  was used to determine coefficient  $n$  which in this case was linear at  $n = 2$ .

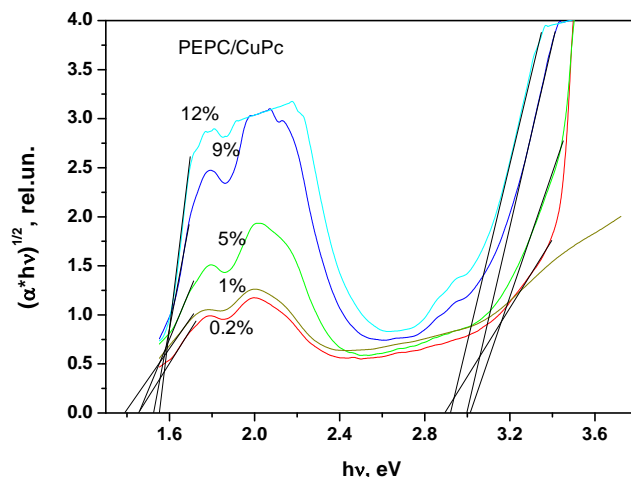
Figure 4 represents the energy dependence of absorption coefficient plotted in the Tauc coordinates  $(\alpha \cdot h\nu)^{1/2} = f(h\nu)$  of the NC. The extrapolation of linear portions of the plots to zero energies yields the energy bands that are presented in Table 1.



**Fig. 3.** Transmission spectra of NCs PEPC/CuPc with CuPc concentrations of in NC of 0.2, 1, 5, and 9 measured immediately after deposition and after treatment with UV light.



**Fig. 4.** Optical absorption spectra of NCs PEPC/CuPc at different concentrations of CuPc in NC measured on fresh samples.



**Fig. 5.** Absorption spectra of NCs PEPC/CuPc at different concentrations of CuPc in NC in coordinates  $(\alpha \cdot hv)^{1/2}$ .

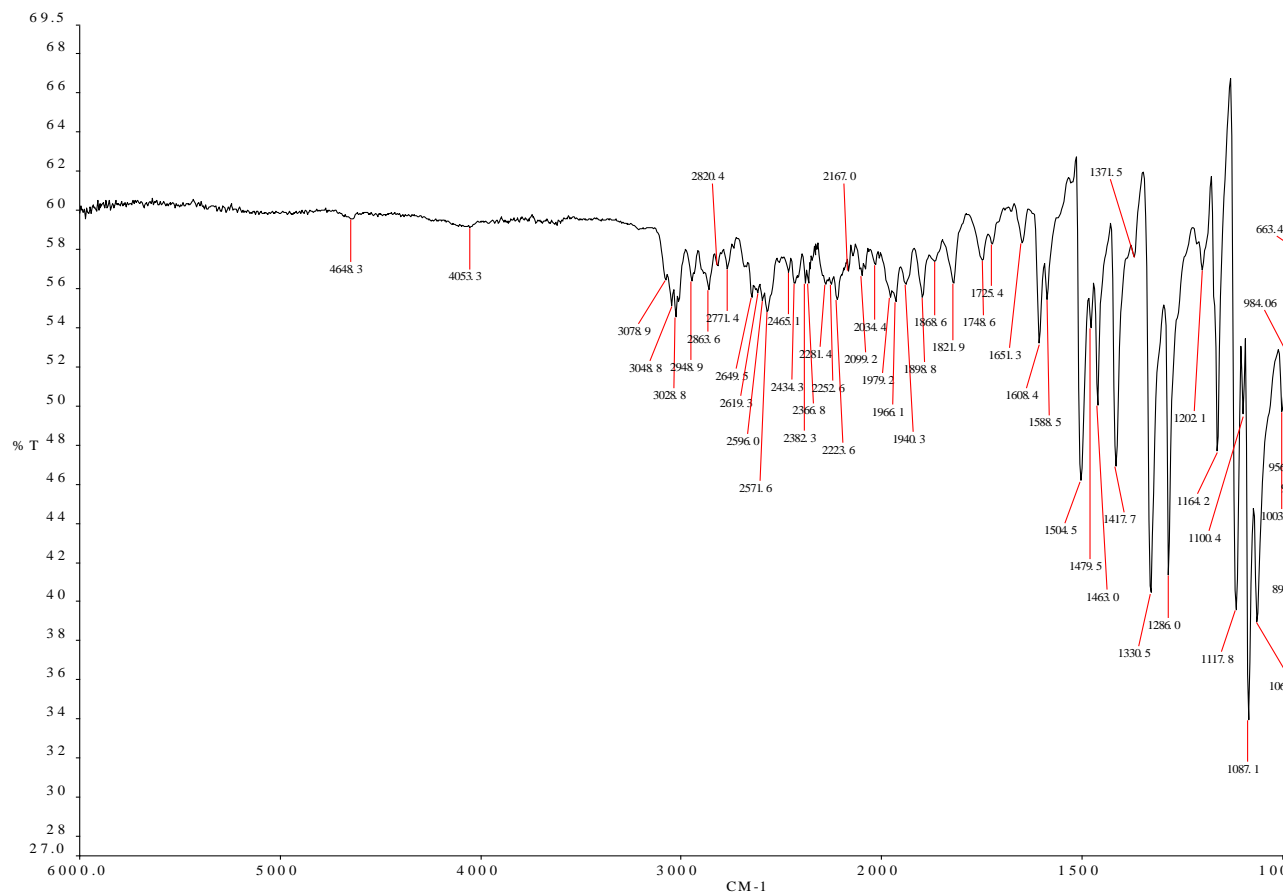
**Table 1.** NC PEPC/CuPc data and maximum of the absorption threshold determined from Fig. 4

Concentration of CuPc in NC, wt %	Threshold energy, eV	Infrared domain of energy, eV	Absorption of Q1, $10^4 \text{ cm}^{-1}$	Absorption of Q2, $10^4 \text{ cm}^{-1}$
0.2	2.88	1.46	0.3	0.2
1	3.02	1.39	0.7	0.5
5		1.46	0.75	0.65
9	3.0	1.53	1.9	1.25
12	3.02	1.55	>5	3.4
	3.0		>5	4.7

To study the structure of the PEPC/CuPc polymeric nanocomposite materials with the organic composite in the solid phase, we measured the infrared (IR) transmission spectra of these compounds by dust on stand in KBr (Fig. 5). From exclusion or difference of these spectra with the same spectra of PEPC, we have highlighted the maxima of characteristics only for the CuPc nanocomposite (Table 2), which are considered to correspond to IR absorption of CuPc compound in NCs. Obtained absorption maxima can probably be attributed to the wave units of CuPc structure (or chemical bonds) of the luminophore compound in NC (C-H, C-N, C-C, Cu-N).

### 3.2. Photoluminescence

The PL spectrum of the PEPC/CuPc nanocomposite is shown in Fig. 6. First, it should be noted that the PL maximum of NCs is shifted to infrared compared to PL of the PEPC layer by about 0.3 eV. Second, PL appears only under excitation of a laser at a wave length of 405 nm. With an increase in the CuPc concentration in NC, the PL intensity decreases. In addition, it is observed that the maximum of PL is less pronounced and the PL is strongly expanded to the infrared up to 1.8 eV. It should be mentioned that the PL spectra measured consecutively show a gradual attenuation of the luminescence. This effect causes a significant quenching of PL. The luminescence spectrum maximum appeared to be decreasing in time, probably due to photochemical reaction after the action of the  $N_2$  laser excitation during measurements.

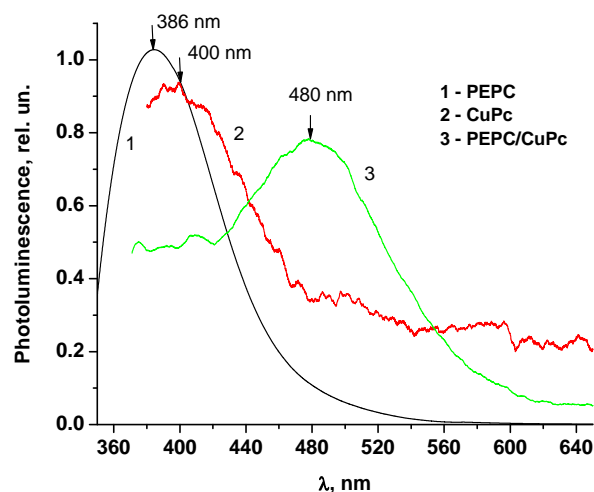


**Fig. 5.** Infrared absorption spectra for the Cu/PEPC nanocomposite.

**Table 2.** Infrared absorption maxima for the nanocomposite organic copper phthalocyanine in NC.

$\nu$ , cm-1	$\nu$ , cm-1	$\nu$ , cm-1
663.49	1065.8	2223.6
679.50	1087.1	2252.6
690.01	1417.7	2281.4
727.38	1463.0	2366.8
752.88	1479.5	2382.3
778.98	1504.5	2434.3
800.75	1588.5	2465.1
876.58	1608.4	2571.6
898.95	1651.3	2596.0
949.70	1725.4	2619.3
956.65	1748.6	2649.5
984.06	1821.9	2771.4
1003.3	1868.6	2820.4
1100.4	1898.8	2863.6
1117.8	1940.3	2948.9
1164.2	1966.1	3028.8
1202.1	1979.2	3048.8

1286.0	2034.4	3078.9
1330.5	2099.2	
1371.5	2167.0	



**Fig. 6.** PL of thin films of PEPC (1), CuPc (2), and PEPC/CuPc nanocomposite (3).

#### 4. Discussion

The absorption spectra of NCs are found to have several maximums; a more complete interpretation of the absorption spectrum and the energy bands is necessary in the future for analysis using a mixed model of Lorentz-Lorentz equations. In our case, this model assumed three oscillator components.

The UV absorption band of the NCs is wide and this can probably be attributed to the overlap of the absorption threshold of CuPc (B) with of PEPC oligomer in the same domain. It is estimated that energy Soret band or tape  $\pi \rightarrow \pi^*$  transitions are caused by the outer circle to the outer circle of phthalocyanine [26] from the molecular orbitals  $\pi$  within the aromatic 18-electron system.

The absorption band in the NIR of visible region for each film sample, which is known as the Q-band representing the  $\pi \rightarrow \pi^*$  transition in the phthalocyanine ring [27] and has a doublet due to Davydov splitting, is positioned at 1.46 and 2.05 eV. The positions of the absorption peaks including the amount of Davydov splitting for the different sample films are different and form an overlapping orbital on the central metal. The extent of Davydov splitting is related to the differences in relative orientation of molecules which are close enough to give electronic transitions, namely, interactions between transition dipole moments from adjacent molecules.

The results of multiple experiments show that the CuPc organic compound present in the PEPC material considerably shifts the luminescence maximum toward the IR wavelength range. For example, Fig. 6 shows a shift of photoluminescence maxima in the red region of the spectra to 480 nm.

The features of PL can be interpreted taking into account the fact that the formation of the nanocomposite leads to an interaction between copper phthalocyanine and the PEPC polymer matrix. This interaction is responsible for the shift of PL maximum from 386 to 480 nm. Under these conditions (UV excitation), the excitation energy from CuPc is transferred to PEPC, where part of this energy is thermalized. This explains the fact that PL is attenuated with increasing

CuPc concentration in nanocomposites.

Another advantage obtained from the CuPc/PEPC nanocomposite is determined by the formation of new absorption bands in an energy range of 1.6–2.4 eV, which leads to additional charge carriers associated with bands. These effects determine an increase of NC photosensitivity in this domain and, consequently, the possibility for application of these materials in storage of optical information. We suppose that the energy transfer from the matrix of oligomer to the CuPc molecule is impossible due to inactivity of chemical bonds between them or because of the presence of thermal transitions.

## 5. Conclusions

We have developed a technology of new composite polymer films based on PEPC nanocomposite oligomer and organic compound of copper phthalocyanine. The optical properties of CuPc thin layers have been investigated by different spectroscopic techniques. It has been found that the absorption spectrum in the deep ultraviolet and visible region consists of three distinct bands, which can be attributed to the intermolecular electronic transitions. PEPC/CuPc polymeric nanocomposites are photosensitive to ultraviolet light and exhibit luminescence in the UV and visible region.

Optical investigations have made it possible to determine the Soret B band gap and Davydov splitting Q1 as well as Q2 bands of CuPc in NC, the maximum absorption coefficient, and the effect of UV irradiation on absorption and band gap. It has been found that the PEPC/CuPc nanocomposite is a material that has an additional absorption in a wavelength range of 600–700 nm. The new nanocomposites can find practical application in different areas of optoelectronics for the development of new registration media, including optical media for holographic storage, electrophotography, photosensors, etc.

**Acknowledgments.** This work was supported by the Institute of Applied Physics of the Academy of Sciences of Moldova (project no. 11.817.05.03A).

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