

# PEPC/CoPc Nanocomposites: Technology and Their Optical Characteristics

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**Abstract** — New type of nanocomposite (NC) films have been fabricated on the basis of  $\pi$ -conjugated oligomer poly-(N-epoxypropyl)carbazole (PEPC) as polymeric matrix and organic compound Cobalt phthalocyanine (CoPc) NC as photochromic dye, and investigated. Thin layers of NC with different concentrations of CoPc in NC (0.2, 1, 3, 6, 9, 12 % of mass) on glass substrates from chemical solutions were deposited. The sizes of CoPc nanoparticles were less than 100 nm. Complex investigation of optical and photoluminescence properties allowed us to determine 3 absorption bands: the absorption band that appears in the region of 315–350 nm and verifies  $\pi \rightarrow \pi^*$  transition for the Soret band B band gap; and  $n \rightarrow \pi^*$  bands appeared at about 600–735 nm for the Q1 and Q2-band. The effect of IR shift of NC under UV irradiation on absorption was observed.

**Index Terms** — nanocomposite, PEPC, Cobalt phthalocyanine, chemical deposition, thin film.

## I. INTRODUCTION

Nanocomposites (NC) based on perspective polymers and organic compounds are excellent structures for a new devices with high performance and use in different areas of optoelectronics, technique, medicine, etc. The main advantages of nanocomposites are their high stability due to fixation and protection of organic compounds and their properties in polymer matrix. They can be obtained in the form of thin layers on large-area and flexible substrates and in the form of fibers or planar waveguides.

One of the interesting and perspectives material are the polymers sensitive to light. Due to the combining of the properties of the photoconductivity and their molecular structure it allow the possibility of achieving of the registration and writing of optical information with high resolution. From this point of view, polymers containing carbazole groups as polymer poly-(N-vinyl)carbazole (PVC) or oligomer poly-(N-epoxypropyl) carbazole (PEPC) presents of particular interest. They possess some important properties as optical transparency, film forming ability, flexibility, thermoplastics, high technology and provide high technology manufacturing sectors at low cost. They are p-type conductivity and are useful for registration of electrographic and holographic media [1-2].

Conduction mechanism in conjugated polymers and compounds on which base are synthesized NC is different from conduction mechanism of conductors or of semiconductors and his peculiarities caused by intermolecular interactions and the possibility of training in them donor-acceptor (D-A) complexes charge transfer. Charge transfer mechanism is the same as in living organisms and form the basis of a method of treating cancer. The polymer layers are as useful tool for researching processes of intermolecular charge transfer

power. The method is based on destruction of cancerlike cell under the action of active O<sub>2</sub>\* (singlet) that form as a result of photochemical reactions in the cell. In the latter case an important role plays the photosensitizer that is introduced and which absorbs the red light passing through the fabric of cell [3]. The photosensitizer bring in such way to increase the sensitivity, optical absorption and the effect of photoconductibility.

Metal organic compounds phthalocyanine MePc presents a particular interest and they are perspective to be introduce in PEPC and to form a composite films with photosensitive properties due their structure with conjugated double bond [4] and to their strong absorption in ultraviolet and visible regions . Metal complexes of phthalocyanine are considering as photoconductors [5], electrophotographic materials [6-7], optical recording media [8] and nonlinear optical materials [9]. Also they have the potential for application in optical logic display devices [10], solar cells [11] and as sensitizers [12]. Photochrome compound CoPc as acceptors for electron are used in NC to form the electronic conductivity, and therefore the doping of thin polymer films are suitable for study of intermolecular electron transfer. Most metal-substituted phthalocyanines have planar molecules. In CoPc, the central metal atom is Cobalt. The major advantage of using organic semiconducting materials is their ability to readily modify their molecular structure, and hence, their electrical and optical properties. However, understanding of phthalocyanine complexes application to composite with polymers was far from complete until now.

In the present paper, we make an effort to synthesize organic Cobalt phthalocyanine compounds and to elaborate a new composite based on it and oligomer PEPC - CoPc/PEPC, and to investigate their optical and

photoluminescence characteristics.

## II. METHODS OF TECHNOLOGY AND UNIT OF EXPERIENCE

Cobalt phthalocyanine has 18  $\pi$  electron of aromatic macrocycle, the structure of molecule is symmetric, flat and consists of four units iminozoinoline. Such macrocycle closely resembles another system met cyclic in nature - porphyrin. For Cobalt phthalocyanine is important the nitrogen atoms which are in the four positions instead of bridges in the presence of the carbon atoms and four benzoic subunits (Fig. 1). Synthesis of the organic CoPc compound was made in the Department of Organic Chemistry at the State University of Moldova. Method of obtaining CoPc [13] is: 42.5 ml of nitrobenzene is added 6.95 g (0.05 mol) of 1,2-dicianobenzen, 0.5 g of Cobalt acetate, 0.002 g of molybdenum oxide (VI). The solution is bubbled with liquid ammoniac, or are adds 1-2 drops of DBU. Reactant mixture is heated to temperature 200 - 300 °C for 3-4 h.

The reaction product (Fig. 1) is cooled down to a temperature range 80 - 85 °C, and at this temperature final product falls as precipitation, then it is filtered through a glass filter. CoPc crystals are washed three times with a volume of 10-15 ml of nitrobenzene heated to 80-90 °C, then with 10 ml of methanol and finally with 25 ml of water. Cobalt phthalocyanine is dissolved well in pyridine and in nitrobenzene hot less.

Chemical structure formulas of poly-(N-epoxypropyl)carbazole is presented on Fig. 2.

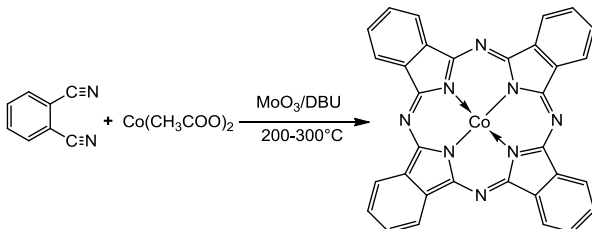


Fig. 1. The technological and chemical structure of phthalocyanine CoPc

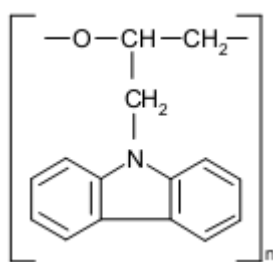


Fig. 2 Chemical structure of poly-(N-epoxypropyl)carbazole.

Thin films of PEPC/CoPc nanocomposites were prepared from chemical solutions. The components of nanocomposite were dissolved separately in pyridine during 24 h, after which they were clasped together and homogenized during 2 h. Thin films deposition ( $d = 1$  mkm) was performed on optical glass by methods of droplets or spin-coating, and then it were dried by complete evaporation of solvent. Samples were obtained with 6 different concentrations of CoPc in NC (0.2%, 1%,

3%, 6%, 9%, 12% of mass). All nanocomposite samples were blue with smooth surface, uniform and transparent.

The morphology of composites was investigated with Linnik microscope MII-4. The obtained samples were transparent and homogeneous, no bubbles or inclusions were observed and this shows that the balls in the polymer are smaller than 0.1  $\mu\text{m}$ , uniformly are distributed and the films can be considered nanocomposites (NC).

The optical transmission spectra ( $T = f(\lambda)$ ) in the range of  $\lambda$  300 - 800 nm were measured using Carl Zeiss Spectrophotometer SPECORD UV-VIS connected to the PC. The photoluminescence spectra were measured using of the monochromator based on MDR-23 connected to PC. The excitation of photoluminescence was performed with a nitrogen laser ( $\lambda = 337.1$  nm) with the radiation intensity of  $P = 0.1-103$  W/cm<sup>2</sup>,  $\tau_1 = 8$  ns) or with Deuterium lamp in the spectral range of  $\lambda = 200 - 500$  nm.

## III. OPTICAL ABSORPTION OF NANOCOMPOSITE THIN FILMS

On Fig. 3 are presented the optical transmission  $T = f(\lambda)$  of thin films of NC PEPC/CoPc for different concentrations of CoPc in NC in the wavelength range 300 - 800 nm. The thickness of all layers on substrates of glass NC was equal to 1 mkm. From transparent spectrum at the high-energy side is highlighted the sharp absorption edge (B) at 330 to 350 nm. The position of absorption threshold B is practically constant and remains with little change at increase the concentration of CoPc in NC.

From the infrared part of spectrum in the range 570-750 nm with increasing concentration of Cobalt phthalocyanine in NC two minimums appear in the transparence (Q1 and Q2). Generally, in wavelength region more than 800 nm the NC films seem to be whole transparent.

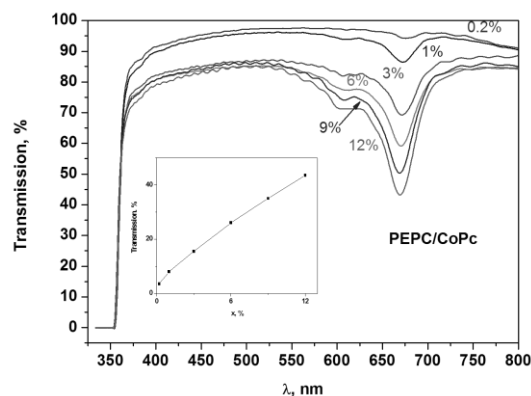


Fig. 3. Optical transmission in NC Pc(Co)/PEPC prepared by the method of droplets without treatment (a), dependence of optical transmission minimum versus concentration CoPc in NC (b).

In Fig. 4 is presented the energy dependence of the absorption ( $a(\text{hy})$ ) obtained from dependence  $T = f(\lambda)$  from Fig ( $a = -\ln T/d$ ). In dependence  $a(\text{hy})$  absorption threshold B is identified that characterize nanocomposites. With increasing concentration the form of the absorption line is changing little. The absorption

maximums of bands Q1 and Q2 are increasing approximately linearly with increasing concentration from 0.2 to 12% (Fig.). The amplitude of maximums absorption of Q1, Q2 increases with increasing concentration and are attributed complete to CoPc in NC.

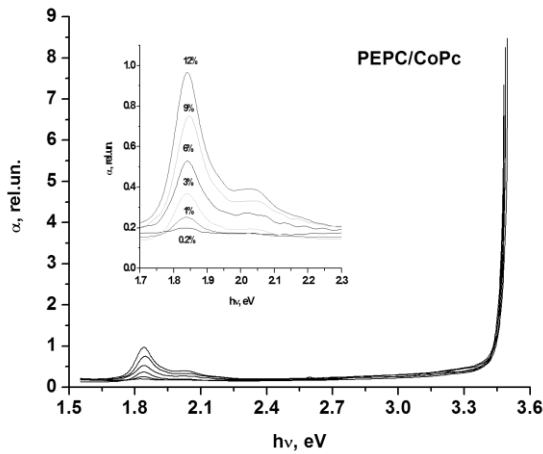


Fig. 4. Absorption spectrum of nanocomposite PEPC/CoPc at different concentrations.

For the energy calculation B, Q1 and Q2 was analyzed energy dependence of absorption coefficient using the formula  $\alpha = \alpha_0 (h\nu - E_i)^n$ , where  $E_i$  is the optical band. The dependence absorption in coordinates  $\lg(\alpha \cdot h\nu) - \lg(h\nu)$  were allowed to determine the coefficient  $n$  which in this case was linear and  $n = 2$ .

Figure 5 represents the energy dependence of absorption coefficient plotted in the Tauc coordinates  $(\alpha h\nu)^{1/n} = f(h\nu)$  of the NC for the sample with a concentration of 12%. The extrapolation of linear parts of graphics to 0 gives the band energy B  $E_B = 3.46$  eV and energies of bands Q1 and Q2  $E_{Q1} = 2.02$  eV and  $E_{Q2} = 1.74$  eV.

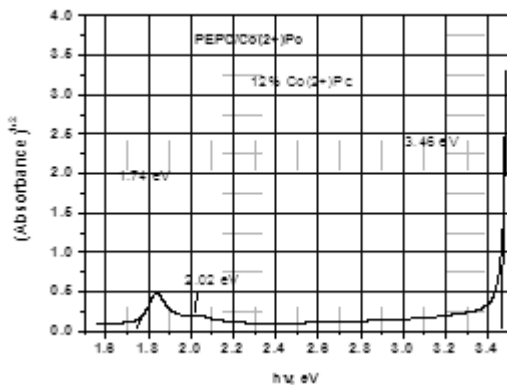


Fig. 5. Absorption spectrum of nanocomposite PEPC/CoPc plotted in the Tauc coordinates.

Probes of PEPC/Pc(Co) were treated with UV light. Spectrum of optical transmission is presented in Fig. 6. We can see in the graphic darkening of NC transparency and shift of minimums Q1 and Q2 to IR. Position of

absorption threshold B at irradiation with UV light remains the same.

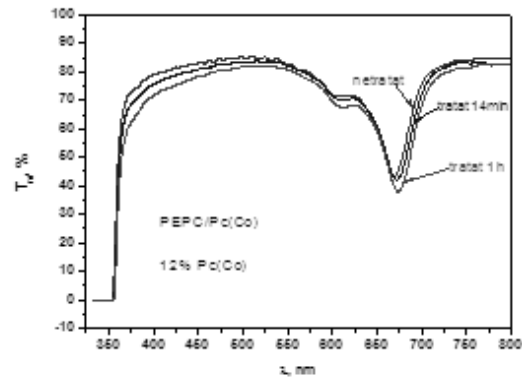


Fig. 6. Optical transmission in NC PEPC/CoPc prepared by the method of droplets with UV treatment during 14 min an 1h

PHOTOLUMINESCENCE OF NANOCOMPOSITES

The photoluminescence spectra of NC PEPC/CoPc at the excitation with a nitrogen laser are presented on Fig.7 for different concentrations of cobalt phthalocyanine in NC in wavelength range 350 – 800 nm. In the dependence of luminescence intensity  $I = f(\lambda)$  of spectrum in the range 350-600 nm have been observed more pronounced two maximums whose positions is the same and stand out up to 380 nm and 420 nm to maintain its position in samples with different concentrations. According of the graph (Fig. 7) the dependence of photoluminescence versus wavelength is asymmetric. The increase of concentration of CoPc from 0.2 to 12% photoluminescence intensity is more than 2 times have decreased.

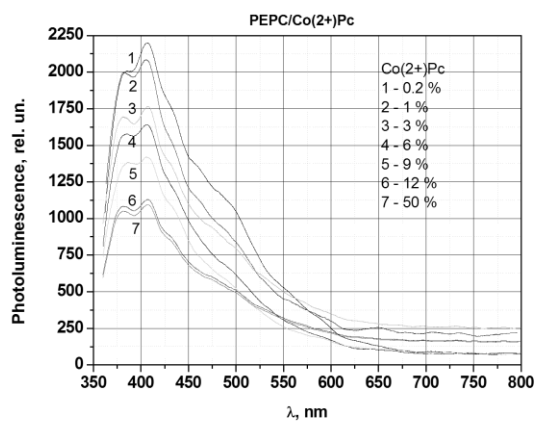


Fig. 7. Photoluminescence spectra of NC PEPC/CoPc dissolved in a toluene solution at different concentrations of CoPc.

It should be mentioned that photoluminescence spectra measured consecutively during time shows a gradual attenuation of the luminescence. This effect cause essential quenching of photoluminescence. The maximum of luminescence spectrum appeared to be decreasing in time, probably due to photochemical reaction after the action of the N<sub>2</sub> laser excitation in during measurement.

#### IV. DISCUSSION OF RESULTS

Spectra of photoluminescence of the nanocomposites in all cases show a well pronounced maximum which is considered to be attributed to the presence of the CH=CH double bond in the polymer and in CoPc compound.

The deviation from the Stokes law of the photoluminescence maximum position to the absorption threshold is in a range of  $h\nu = 0.1 - 0.15$  eV. This deviation can be explained by the presence of a hydroxyl group in compound CoPc.

The optical absorption spectra for 1 μm film thicknesses of CoPc are given in Fig. 5. The spectrum originates from orbitals within have been confirmed for many the phthalocyanine complexes and is related to the formation of singlet excitons [6-9].

The absorbance spectrum shows sharp increase in absorption at wavelength near the absorption edge of the threshold wavelength of the absorbance spectrum, the energy corresponds to this determines the optical band gap of the semiconductor material. The spectrum originates from orbitals within the been confirmed for CoPc phthalocyanine complexes and is related to the formation of singlet excitons. The absorption at the lower energy side is related to singlet excitons of D-A central ion Co with nitrogen ions [14].

The data of the absorption spectra obtained verifies that  $\pi$ - $\pi^*$  transition appears in the region of 315–350 nm for the Soret band and  $n - \pi^*$  appeared at about 600– 735 nm for the Q-band. [14].

Optical properties of NC films are controlled by energy band gap and the trap levels present in the forbidden energy gap. Since the interactions of Cobalt phthalocyanine molecules are of Vander Waals type, the rearrangements of molecule alter the energy band gap between valence band and conduction band.

In articles [14] were performed calculations and ab initio calculation of the total energy from electronic structure of CoPc was established, and recent interest had moved to evaluation of free energies and equation of state [14]. The  $\pi - \pi^*$  transition appears in the region of the Soret band. This band was appeared at 346 nm of phthalocyanine and shifted to 315 nm for CoPc [29].

Generally authors noticed that, the Soret band was shifted to shorter wavelength related to phtalocianine with increasing the number of electron in the 3d orbital for the bivalent cations  $Co^{2+}$ .

The most essential characteristic of the charge-transfer CoPc was the double chain and two-band structure: a metal d-chain and macrocycle p-chain coexists within the same molecular column and a narrow 3d-band was located near the Fermi level of a wide  $\pi$ -band [11]. It has been suggested that, the VIS spectrum obtained for (CoPc) originates from the molecular orbital within aromatic 18  $\pi$  electron system and from overlapping on central metal ions [12].

The model proposed for explanation, which describes the photochromic changes in the photoemission spectra nanocomposite polymer, envisaged conditions of excitation and proton transfer in P EPC/CoPc nanocomposites. According to this model, the protons are transferred in the excited state of carbon from nitrogen position. For this excitation, the first singlet status of

arousal is considered to be a strictly acidic state and the state of "nitrogen" is strictly basic. Thus, the isomer ( $S^*$ ) is formed, which in this case is more stable than the isomer (S) until the proton transfer. So, the state  $S^*$  can be considered as an excited vibrational state S. After transition of the molecule in normal state one is emitted a photon. In the result of this process, the proton is transferred back to the state of carbon, which is more stable state in this case. It can be considered that the reverse state S is also excited by the vibrational state  $S^*$ .

#### V. CONCLUSION

A new technique for thin film nanocomposites PEPC/CoPc by a chemical method was developed and their physical properties were characterized by microscopic measurements, transmission and photoluminescence spectra.

Optical studies are allowed to determine the B band gap and Q1 si Q2 bands of NC, maximum absorption coefficient and the effect of UV irradiation on absorbtion and band gap.

From experimental data it was found that NC PEPC/CoPc is a material that have an addition absorption in wavelength range 600 - 700 nm. These properties allow the use given to manufacture photosensitive composite for devices operating in this field of energy.

The obtained nanocomposite films are promising materials for the preparation of various fluorescent and photosensitive dyes and devices. These nanocomposites can be applied in various areas of engineering and optoelectronics as indicators of UV irradiation and rigid irradiation, for converting these energies in the visible spectra, as electrophotographic and holographic media for recording of optical information, etc.

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