

# Energy Transfer in Organic Luminophore Nanocomposites

V. Verlan<sup>1</sup>, A.M. Andriesh<sup>1</sup>, I. Culeac<sup>1</sup>, A. Popushoi<sup>2</sup>, G. Dragalin<sup>2</sup>, N. Barbă<sup>2</sup>, S. Buzurniuc<sup>1</sup>, L. Malahov<sup>3</sup>

<sup>1</sup>Institute of Applied Physics of Academy of Sciences of Moldova, 5 Academiei Str., MD-2028 Chisinau, Republic of Moldova.

<sup>2</sup>State University of Moldova, 60, Mateevici Str., MD-2009 Chisinau, Republic of Moldova

<sup>3</sup>Institute of Mathematics of ASM, 5 Academiei Str., MD-2028 Chisinau, Republic of Moldova.

Corresponding author: [vverlan@mail.md](mailto:vverlan@mail.md)

**Abstract** — New light-emitting layers of nanocomposites on polymer base have been obtained. As polymeric matrices the poly-N-vinylpyrrolidone has been used. As organic luminophore materials new compound from izotiocianatopropenone classes 3-(anthracen-9-il)-1-(4-izotiocianatofenil)-prop-2-en-1-one (ANA-CH) were utilized. Transparent composite layers were deposited by spin-coating method on glass and quartz substrates. The morphological, optical and photoluminescence properties of the obtained nanocomposites have been investigated. An intensive photoluminescence signal has been identified in green area of the spectrum. His proposed the model of energy transfer in NC from the polymer matrix to ANA-CH luminescence centers. Nanocomposites are proposed for various practical applications.

**Key words:** Nanocomposites, organic luminophore material, luminescence

## 1. INTRODUCTION

Nanocomposites (NC) based on polymers and organic luminophore compounds (OLC) are excellent materials for a new generation of light emitting devices with high efficiency due to strong luminescence, easy color tunable, temperature insensitivity, and high stability. There are real perspectives for their applications in different optical devices, for example, for preparation of different dyes and fluorescing devices (especial for fabrication of luminescent screens and fibers), of light amplifying devices, converters of the UV light in visible, etc.

The paper presents new results on thin film nanocomposites of organic luminophore polymer compounds prepared by sol-gel method. The poly-N-vinylpyrrolidone was used as polymeric matrix. As organic luminophore compound we have applied new compound from isothiocianatohalonic luminophore group.

## 2. METHODOLOGY

Luminophore components of nanocomposites were obtained at the Department of Organic Chemistry of the State University of Moldova Republic. The scheme of technology and chemical structures of organic luminophore compound ANA-CH are shown on (Fig. 1).

The obtaining method of 3-(anthracene-9-yl)-1-(4-izotiocianatofenil)-prop-2-en-1-one (ANA-CH), consist in elimination of dimetilamine from 3-(4-(3-(anthracene-9-il) acriloil) phenil)-1.1-dimetiltiurea (1) at the boiling in chloroform and action with acidic agents with acetyl chloride (I) and acetic anhydride (II) according to the following schedule:

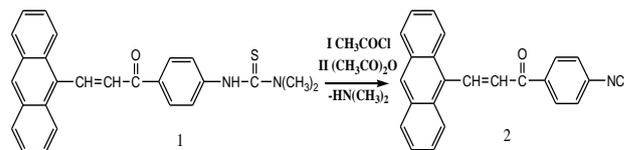


Fig. 1. The scheme of technology and chemical structures of organic luminophore compound ANA-CH.

As result it was obtained 3-(anthracene-9-il)-1-(4-izotiocianatofenil)-prop-2-en-1-one (2) with yields of 94% (II) and 80% (I). The structure of 3-(anthracene-9-yl)-1-(4-izotiocianatofenil)-prop-2-en-1-one (2) was confirmed by spectral analysis (<sup>13</sup>C-RMN). The structure of compound ANA-CH was confirmed also by elemental analysis, IR spectra and reactions to functional groups.

<sup>13</sup>C-RMN (DMSO-d<sub>6</sub>), ppm: 179.70 (C=O), 139.75 (C-N), 149.38 (-CH=CH), 121.49 (-CH=CH-), 137.34 (-C<sub>6</sub>H<sub>4</sub>-N=C=S), 125.83, 122.92.

The nanocomposites on the base of the poly-N-vinylpyrrolidone PVP/ANA-CH were prepared from chemical solutions. The detailed method of NC preparation was described in [1]. The components of NC were dissolved in dimethylformamide, and then colloidal suspension of the solution was mixed and stirred during of 3 hours. Thin layers on glass or quartz substrata were deposited by spin-coating method and then dried. The organic luminophore complexes was successfully incorporated with different molar ratios (0.5% – 20%) into organic polymer matrix of PVP. For all nanocomposites the sample color was yellow-orange. The dried layers turn out to be transparent. A series of thin films with the thickness from 0.2 µm to 2.0 µm and concentrations of organic luminophore compounds in NC from 0.2% to 20% have been prepared. The morphological properties of obtained composites were investigated using the microscope MII-4.

For optical transmission spectra measurements, SPECORD UV/VIS (0.4-0.8  $\mu\text{m}$ ) of CARL ZEISS JENA and Perkin Elmer Spectrum 100 FT-IR spectrometers equipment were used. The photoluminescence spectra have been measured using a set-up based on MDR-23 and DFS-24 monochromators connected to PC. The excitation of fluorescence has been carried out by the nitrogen laser ( $\lambda=337\text{ nm}$ ) with intensity of radiation in range  $0.1 - 10^3\text{ W/cm}^2$  or Deuterium lamp in the spectral range of 250 – 800 nm.

### 3. EXPERIMENTAL RESULTS

The microscopic investigations of the morphology of the NC surface on a MII-4 microscope show that the dimensions of luminophore organic compounds particles incorporated in the polymer matrix are invisible and hence are less than 100 nm. And because the colours of NC layers are stable and not dependent on the technology or on the method of incorporation into the matrix of polymer it follows that the sizes of particles are larger than 6 - 10 nm when their colour are usually sensitive on dimensions of particles. The microscope investigations also reveal that ANA-CH complexes are dispersed in PVP homogeneously without any phase separation. Thin films of NC PVP/ANA-CH have an intensive green luminescence under ultraviolet light excitation.

The transmission ( $T(\lambda)$ ) spectra in the infrared (IR) domain of spectra were measured on the powders of OLC and NC PVP/ANA-CH. The absorption maximums were obtained at:  $\text{cm}^{-1}$ , 644, 812, 1300-1305, 1339-1342, 1522-1534, 1598-1602, 3027, 3374-3285, 3041, which as we suppose correspond to the organic compound luminophore 3-(anthracene-9-yl)-1-(4-izotiocianatofenil)-prop-2-en-1-one (2). The obtained maximums of absorption can be most probably attributed of the structural units of organic luminophore compounds from the nanocomposite: N-H, N-R, C-S, N-S, N-CH<sub>2</sub> and which increase with increasing concentration of luminophore compounds in NC.

Transmission spectra  $T(\lambda)$  of thin layers of nanocomposite PVP/ANA-CH, both the glass substrate and layer PVP on quartz substrate in the ultraviolet and visible region of spectrum at different concentrations of OCC in NC are presented in Fig. 4. The sharp absorption thresholds are presented for all concentrations of coordination compounds in NC in the range of 200 - 500 nm of spectrum. The energetic position of the absorbance maximums of NC remains constant with increasing of concentrations of organic compounds, but the absorption increases without reaching the saturation. The absorption coefficient of spectra  $\alpha(\lambda)$  is calculated from the transmission spectra  $T(\lambda)$  through the relation  $\alpha(\lambda) = -\ln T/d$  (where  $d$  is the thickness of NC,  $\alpha$  – absorption coefficient). The layers of polymer PVP without the luminophore additives was transparent in visible and near ultra-violet areas of a spectrum. In thin films nanocomposite a number absorption bands positioned at 2.5, 3.0; 3.9; 4.8; 5.5 eV have been found. The most intensive band of absorption can be seen at 2.5 eV. The spectrum of absorbance of NC PVP/ANA-CH at different

concentrations of OLC in NC on glass substrate is shown in Fig. 5.

Photoluminescence spectra for different concentrations of OLC ANA-CH CN are presented in Fig.4. Note that with increasing of the concentration of OLC in NC the intensity of photoluminescence peak deviates from 2.38 eV at 0.5% to 2.22 eV at 15%. Starting with 10% concentration the maximum of intensity decreases sharply. This attenuation probably is caused of decrease specific surface of particles embedded in polymer matrix and with increase the transitions nonradiative of the energy transfer from the polymer at OLC.

The Stokes displacements of luminescence are 0.12 – 0.28 eV. The value of Stokes shifts can be explained by the presence of a hydroxyl group. The model for explanation of Stokes displacement is proposed which takes into account the excited conditions and transfer of a protons in molecules containing fragments of anthracene and oxygen. According to this model the proton is transferred from the oxygen site to the anthracene site. Then the molecule de-excites to the ground state, emitting a photon. During this process proton is transferred back to the oxygen site.

Fig. 5 shows the photoluminescence kinetics of nanocomposites PVP/ANA-CH at temperatures 298 K. Note two slopes in the experimental plot  $\ln I(t)$  for the relaxation mechanism described by the relation of type  $I = I_{01}\exp(-t/t_{01}) + I_{02}\exp(-t/t_{02})$  with two characteristic relaxation times 0.3 and 10  $\mu\text{s}$  at temperature 298 K. The detailed analysis of experimental data shows that the magnitude of characteristic time  $t_{01}$  (0.5  $\mu\text{s}$ ) is less than the measurement error, and therefore we can assume that this characteristic time value is less than  $10^{-8}$  s. The second relaxation time  $t_{02}$  (2.5  $\mu\text{s}$ ) that can be easily observed in the relaxation characteristics we suppose can be attributed to the mechanism of phosphorescence.

Temperature dependence of maximum of photoluminescence intensity at 556 nm is linear. From the slope of this line was 12.7 eV found the activating energy which is attributed to photoluminescence excitation process with ultraviolet light.

The model of photoexcitation and proton transfer in molecules containing fragments of protons was used to describe the photochromic change in the emission spectra of polymer nanocomposites. According to this model, the proton remains predominantly on the anthracene site. Upon UV excitation, in the first excited singlet state, the “phenil” is a considerably stronger acid and the “oxygen-site” is a stronger base. Thus, the proton is transferred from the anthracene site to the oxygen site, and the formed isomer ( $S^*$ ) is more stable than the isomer before proton transfer ( $S$ ).  $S^*$  can be then regarded as a vibrationally excited form of  $S$ . Next the molecule de-excites to the ground state, emitting a photon. In the ground state the “enil” site is again the more stable form and the proton will then transfer back to the oxygen.  $S$  is also a vibrationally excited state of  $S^*$ .

The Gaussian character of distribution of photoluminescence intensity in the NC remains the same with increasing the content of organic compounds in NC up to 20%. It should be mentioned that comparison of

PL in NC luminophores and layers of organic compounds at the same conditions of excitation shows that the photoluminescence signal in nanocomposites is several times higher than in organic compounds.

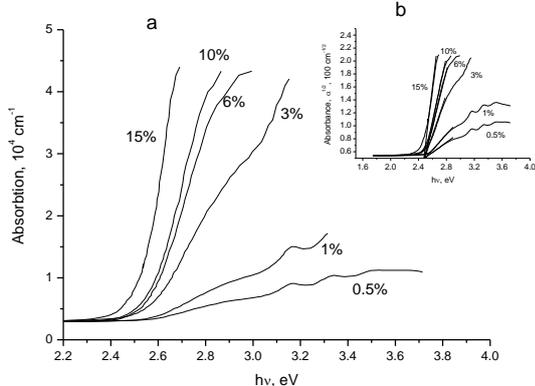


Fig. 2a,b. The absorbance spectra of NC PVP/ANA-CH at different concentrations of OLC in NC.

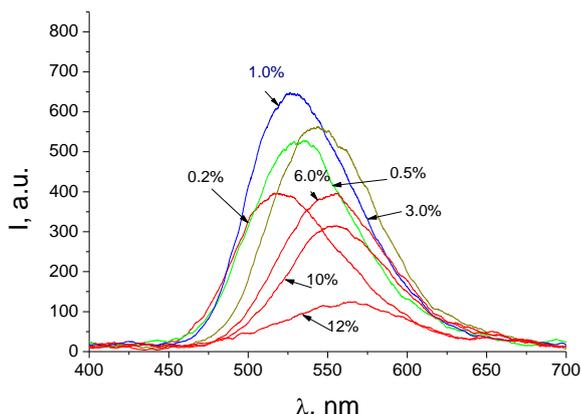


Fig. 3. The photoluminescence spectra of NC PVP/ANA-CH at different OLC in NC.

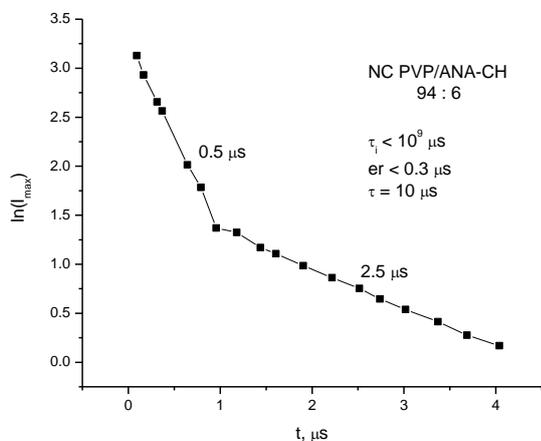


Fig.4. The kinetic dependency of the intensity maximum for NC PVP/ANA-CH.

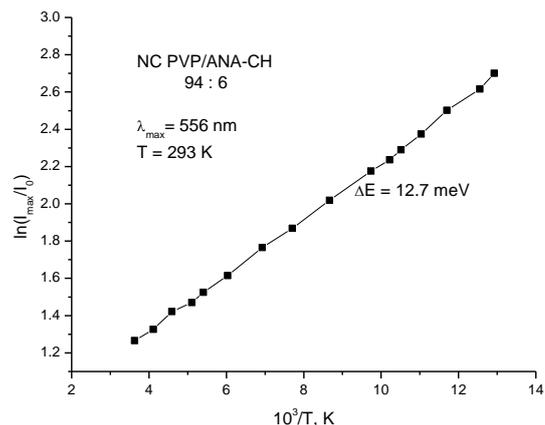


Fig.5. Temperature dependency of the intensity maximum for NC PVP/ANA-CH.

#### 4. Conclusions

New luminophore nanocomposites have been prepared on the basis of polymer polyvinyl-N-pyrrolidone and new organic luminophore 3-(*antracen-9-il*)-1-(4-*izotiocianatofenil*)-*prop-2-en-1-one*. The basic parameters describing the luminescence are determined: the spectral range of photoluminescence and energy of maxima of the radiated centres.

The model of the excited-state proton transfer in molecules containing fragments of has been used for the description of photochromic shift in emission spectra of polymer solutions and films.

The studied composites are promising materials for the preparation of different dyes and fluorescing devices. These investigations are especially interested for fabrication of luminescent displays and fibers. It is expected that at optimal concentration of organic luminophore compound in the fiber from nanocomposites (1 - 5 % by mass) the resulting NC will have intensive fluoresces properties. Received NC can be used also in various areas of optoelectronic and engineering: as indicators of UV and rigid radiation, for conversion of the UV energies to visible spectrum, as well as amplifiers and modulators of light, etc.

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