JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 10, No. 12, December 2008, p. 3353 - 3356

Fluorescent properties of nanocomposite organic luminophore compound – polymer

A. ANDRIESH[a], S. BUZURNIUC[a], V. VERLAN[a*], M.I. CARAMAN[b], S. ROBU[b], N. BARBĂ[b]
[a]*Center of Optoelectronics of IAP of Academy of Sciences of Moldova*
[b]*State University of Moldova*

Thin luminofore layers of nanocomposites (NC) on a base of copolymer styrene and butylmethacrilate (SBMA) and of organic luminofores 5-(4-dimethylamino-benzylidene)-pyrimidine-2,4,6-trione (PI) or 3-(4-dimethylamino-phenyl)-1-(4-isothiocyanato-phenyl)-propenone (PII) are obtained. The dimensions of PI and PII particles are less than 100 nm and they are uniformly distributed in a matrix of polymer. The absorption of NC reveals bands of absorption with maxima at 470, 432 and 340 nm for PI-SBMA and 443 nm for PII-SBMA. The photoluminescence (PL) of NC reveals an intensive wide band at 532 nm for PI-SBMA and 5 bands at 450, 490, 518, 640 and 700 nm for PII-SBMA.

(Received November 5, 2008 ; accepted November 27, 2008)

Keywords: Nanocomposites, Luminofores, Optical amplifiers

1. Introduction

The phenomena of transformation of photon energy in material under UV irradiation, so-called photochromatisme have been attracted the attention of researchers and engineers during more than 40 years. This is connected with real perspectives for their using in different optical devices. At present there are high interest for obtaining and investigation of the nanocomposites of luminophore materials. This is connected with the multifunctional properties of composites in which are included two compounds and the possibility for preparation on their base different dyed and fluorescing devices, especial for fabrication of the luminophore and electroluminophore screens and fibres, amplifyings of the light , transformations of the UV light to visible, photoinduced phenomena, photoluminescence, etc.

In present work we present the investigations of organic luminophore/organic material nanocomposites, particularly, those prepared by the sol-gel method. As polymer matrix, it were used copolymers from styrene and butylmethacrilate (SBMA) in ratio (1:1) with characteristic viscosity η= 0.29 Dl. In the first case the organic luminophore compound obtained at condensation of 5-(4-dimethylamino-benzylidene)-pyrimidine-2,4,6-trione with barbituric acid in base medium (PI) [1] was used:

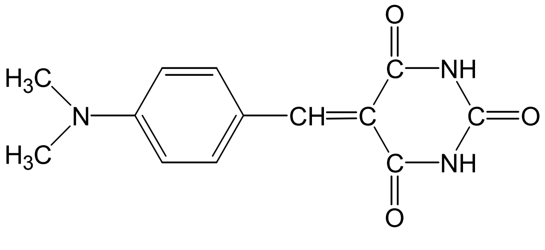

Fig.1. 5-(4-dymethylamino-benzylidene) -pyrimidine-2,4,6-trione

In the second case the isothiocianatohalconic luminophore 3-(4-dimethylamino-phenyl)-1-(4-isothiocyanato-phenyl)-propenone (PII) was obtained by condensation 1,1-dimetyl 3-(3- or 4 –acetylphenyl) thiourea with substitutioned aromatic aldehide [2] according of the schema:

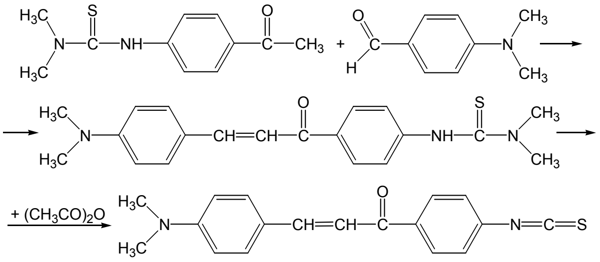

Fig.2. Scheme of obtaining of the isothiocianatohalconic luminophore

Both components of nanocomposites were obtained at the Department of Organic Chemistry of the State University of Moldova Republic. The components of nanocomposites were dissolved in organic solvents then colloidal suspension of the solutions were mixed and homogenated. The thin layers on glass substrate were deposited by spin-coating method [3, 4] and then dried. A series of films with the thickness in range 0.2 – 2.0 μm have been prepared.

The morphological properties of the obtained composites by using microscope MII-4 were investigated. The layers turn out to be transparent. For composite PI-SBMA the colours were yellow - orange and for composite PII-SBMA was orange. Depending of the luminophore concentrations the dimensions of the spheroids were less than 0.1 μm and did not observed in microscope. From such fact we conclude that the particles have nanodimensions. For optical transmission spectra measurements, SPECORD UV/VIS (0.4-0.8 μm) and SPECORD 61 NIR (0.8-3.2 μm), CARL ZEISS JENA equipment were used. The excitation of fluorescence was carried out by the nitrogen laser (0.337 nm) with intensity of radiation in range 0.1 - 10^3 W/cm^2. The absorption and fluorescence spectra of these polymers have been studied by using time-resolved fluorescence technique.

The obtained thin layers of SBMA polymer are transparent in whole domain of investigated spectra (visible and infrared). In the absorption spectra (Fig.3,4) of nanocomposites PI-SBMA are pronounced bands with maxima at 470, 432 and 340 nm (Fig.3). After the increasing of the photoluminophore concentration in nanocomposites the intensity of absorption maximum at 2.80 eV with Gauss distribution character increased sharply.

The photoluminescence spectra are shown on Fig 5 for PI-SBMA. The PL spectra show well pronounced maximum at 532 nm with halfwidth 117 nm and 37 nm at temperatures 78 and 293 K respectively. When increasing the temperature the positions of the maxima are almost constant. We considered that the maximum of absorption at 529 nm corresponds to the photoluminescence maximum at 532 nm.

The PL spectra of NC PII-SBMA are shown on Fig. 6 at two temperatures. Some maxima at 450, 490, 518, 640 and 700 nm were detected. It is necessary to mention that with variation of the temperature the position of the main maximum does not change essential.

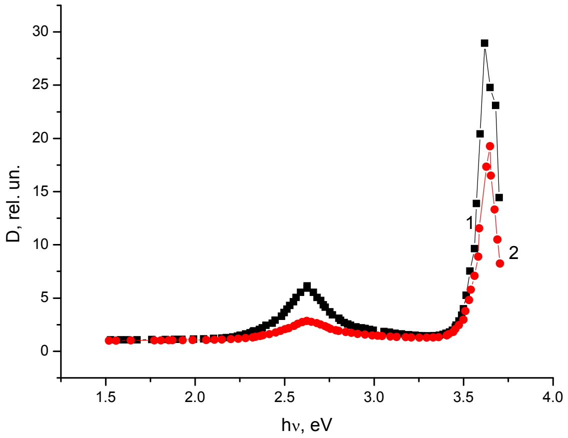

Fig.3. Energy dependence of optical density for nanocomposite P1-SBMA and 2 concentrations of PI (0.5% (1) and 1% (2)).

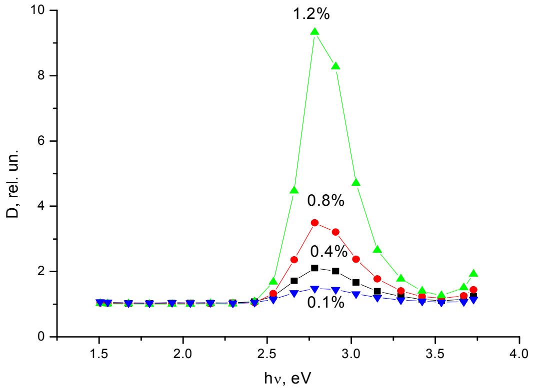

Fig. 4. Energy dependence of optical density for nanocomposite PII-SBMA and different concentrations of PII in nanocomposite

On fig. 7.8 are presented the temperature dependences of the maxima intensity of a photoluminescence of composites PI(PII)-SBMA. In coordinates $\ln I_{max}$ - $10^3/T$ dependences are rectilinear. For these temperature dependences of the intensity maxima in NC PII-SBMA at 650 nm are found out two levels with energies 5.5 meV and 21.6 meV and at 450 nm levels 10 meV and 21.6 meV.

In NC PI-SBMA from same dependence of the maximum of intensity at 505 nm are revealed only one rectilinear inclination corresponding to the energy 12.7 meV.

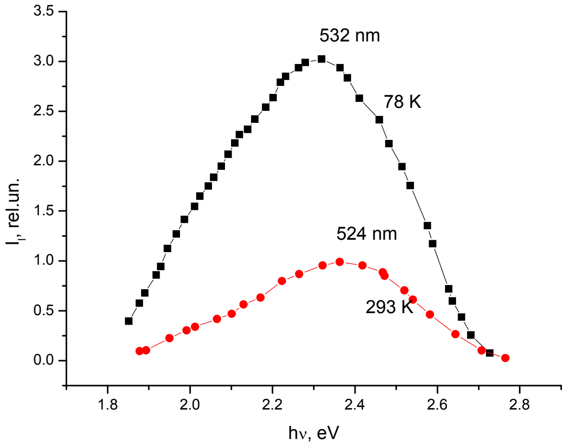

Fig.5. Photoluminescence spectra of P1-SBMA. at 78 and 293 K.

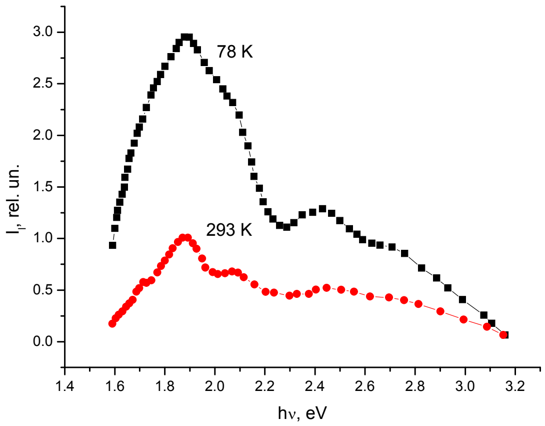

Fig.6. Photoluminescence spectra of PI1-SBMA. at 78 K and 293 K.

The kinetics of the decay of maxima of the photoluminescence after the excitation interruption is shown on Fig.5. The dependence $I_{max}(t)$ can be described by $I_0 exp\ (t/\tau_0)$, where τ_0 is life time of the exited state. For PII-SBMA τ_0 are of 0.3 and 10 μs for a maximum 450 nm and 0.5 and 2.5 μs for the second maximum at 650 nm.

The high value of Stokes shifts can be explained by the presence of a hydroxyl group. A model for analyzing the Stokes displacement is proposed which takes into account the exited conditions and transfer of a protons in molecules containing fragments of 4-dimetilaminobenzoice. According to this model the proton is transferred from the oxygen site to the nitrogen one. Then the molecule de-excites to the ground state, emitting a photon. During this process proton is transferred back to the oxygen site.

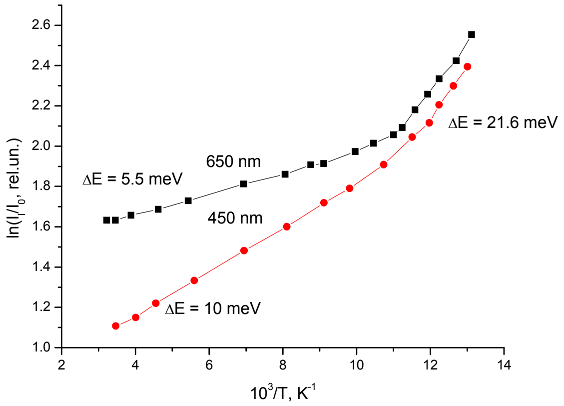

Fig.7. Temperature dependency of the intensity maximum for NC PI-SBMA.

We consider that special behavior of NC and the high value of Stokes displacement are caused of the presence of hydroxyl group in initial position *ortho* and their interaction under excitation with N atom of the benzoxasole ring. Probably, there are the transfer of proton (or, better says, of the charge of hydrogen) in direction of molecules fragments which contain nitrogen. The small τ_0 value demonstrate that this process is connected with the changing of electronic level connected with displacement of its orbital state and with formation for a short time an instable isomer, which after interrupting of excitation return to the initial state.

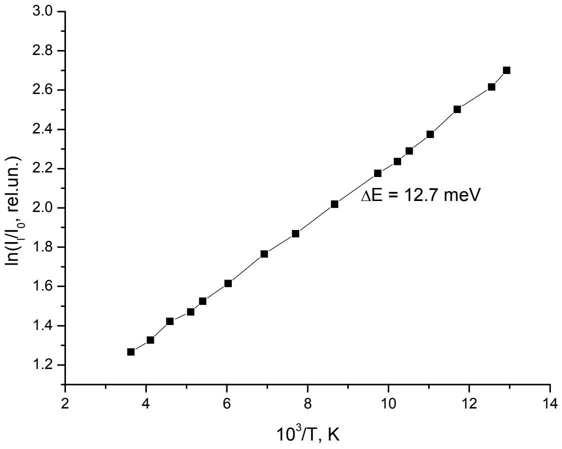

Fig. 8. Temperature dependency of the intensity maximum for NC PII-SBMA.

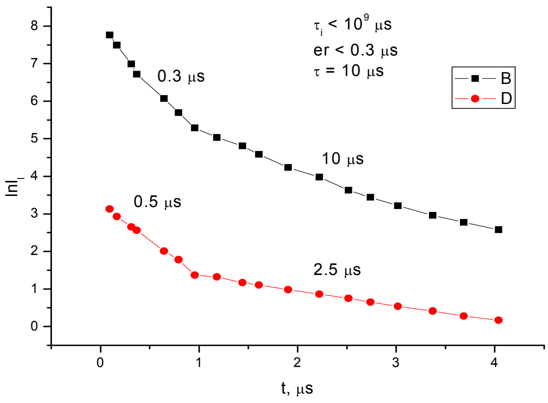

Fig.9. Kinetics decay of the maximum intensity of photoluminescence for NC PII-SBMA. I_{max}: B at 450 nm and D at 650 nm

2. Conclusions

We have obtained new luminophore nanocomposites on the base of copolymer styrene and butylmethacrilate and of organic luminofores 5-(4-dimethylamino-benzylidene)-pyrimidine-2,4,6-trione (PI) or 3-(4-dimethylamino-phenyl)-1-(4-isothiocyanato-phenyl)-propenone (PII) and have investigated of their absorption and fluorescence properties.

It was found that the special feature is the large value of Stokes shift due to the presence of a hydroxyl group in the *ortho*-position to the nitrogen atom of the bensoxasole ring.

Upon UV excitation, in the first excited singlet state, the "phenil" is a considerably stronger acid and the "nitrogen" is a stronger base. Thus, the proton is transferred from the oxygen site to the nitrogen site, and the isomer formed (S*) is more stable than the isomer before proton transfer (S). S* can be then regarded as a vibrationally excited form of S. Then the molecule de-excites, to the ground state by emitting a photon. In the ground state the "enil" form is again the more stable and the proton will then transfer back to the oxygen. S is also a vibrationally excited state of S*.

The basic parameters describing the luminescence are determined: range of PL, energy of maxima, the temperature dependence, and life time of the radiated centres.

The nanocomposite can be used in various areas of engineering: as indicators of UV and rigid radiation by transferring these energies in visible areas, as amplifiers, modulators of light, etc.

References

[1] To be published.

[2] N. Barbă, Gh. Luchiță, A. Barbă, R. Vieru. Brevet de invenție MD nr 2985 publicat in BOPI nr 2 (2006).

[3] S.A.Buzurniuc, V.I. Verlan. Technology of thin films deposition of organic polymer/amorphous inorganic compound composites. "3-rd International conference on materials science and condensed matter physics", Abstracts MSCMP p. 141, (2006).

[4] V. Verlan, S. Buzurniuc, S. Robu, N. Barba, M. Caraman, Ac. A. Andriesh. Some fluorescents properties of organic/organic composite on base of luminopfor compound and polymer. "3-rd, International conference on materials science and condensed matter physics", Abstracts MSCMP p. 118, (2006).

---

*Corresponding author: vverlan@mail.md