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VISIBLE AND NEAR INFRARED EMISSION OF POLYMER MATERIALS CONTAINING PORPHYRIN AND ITS YTTERBIUM DERIVATIVE.

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A series of porphyrin containing polymer materials of various structure was developed. Free 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrinand its ytterbium derivative were used to prepare materials of different structure and they were obtained by different approaches. Thus, two polymers were used in this study – the poly(methyl methacrylate) (PMMA), polystyrene (PS) as well as their copolymers of different composition (the molar ratio of 0.25/0.75, 0.5/0.5 and 0.75/0.25). Also part of materials were obtained by coprecipitation of polymer(s) with corresponding porphyrin derivative. The latter material ismore transparent, which allows obtaining an absorption spectrum with good resolution. All materials have notable emission characteristics – they emit in visible or near infrared (IR) range. Increasing of PMMA content in the final material causes the increase of fluorescence quantum yield for bothcopolymers and coprecipitated materials.It can be explained by a higher light transmission coefficient of PMMA compared to PS.It was found out that *4f*-luminescence in ytterbium-containing materialsdoes not depend on the type of polymer matrix and the variability of its compositionin contrast to fluorescence in the visible range.Almost 100% transparency of the studied polymers in the area of ytterbium ion radiation (980 nm)explains this phenomenon. It was also shown that obtainedmaterialsare stablefora long period of time and they keep the permanence oftheir emission parameters.This phenomenon can be explained by the extraordinary stability of PMMA even to UV radiation and by the high stability of porphyrin molecules. The use of a low concentration (0.1%) of lanthanide-porphyrin in the final material allows the IR emission efficiency of the Yb(III) ion to remain at the same level as in the corresponding methanol solution.

Keywords: polymers; lanthanides; porphyrins; fluorescence; *4f*-luminescence.

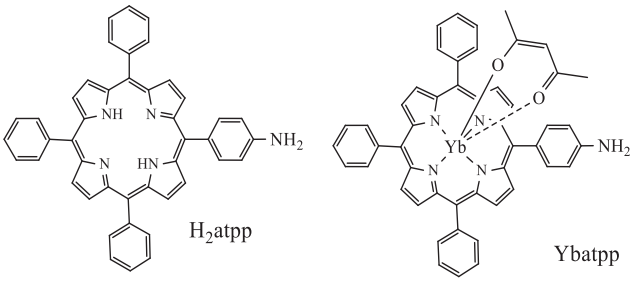
INTRODUCTION. Tetrapyrrole derivatives such as porphyrins, phthalocyanines and porpholactones are highly stable macrocyclic compounds that play an important role in many biochemical phenomena related to the development of life [1–3]. Their complexes with lanthanides have special properties, such as paramagnetism, nonlinear optical parameters and intense light emission in the visible and near-IR ranges[4]. Many studies focuses on their bioimaging capabilities and as sensors. [5]. Also, recently there has been an increase of works devoted to the sensitization of lanthanide ions emitting in the near-IR region of the spectrum [6–8]. In addition, IR radiation is an extremely effective tool for protecting securities and banknotes from counterfeiting [9]. The increase in the quantum yield of *4f*-luminescence of Yb(III)-tetrapyrrole complexes in the IR range achieved in recent years[10] reflects the viability of these studies and open up opportunities for their use not only in the medical and biological aspect, but also as materials for optoelectronics.

In the modern context, porphyrin polymers are widely used to solve different problems in various fields of science and technology [11–13]. Immobilization of porphyrins on a polymer provides several advantages that are not present in free compounds. Among them, it is worth noting cooperative interactions in polymer chains, separation of active centers, the possibility of specific binding of various substrates on active centers, increasing the stability of tetrapyrrole pigment, as well as reducing its toxicity relative to biological environments.

These systems are promising as highly selective catalysts, organic semiconductors, polymer films with high electrical conductivity, light-sensitive materials for recording holographic images, as well as sensors for oxygen and toxic gases [14, 15]. Currently, medicine and pharmacology are among the promising fields of application of porphyrin polymers. In recent years, therehas appeared an information about the possibility of using polymer porphyrin systems for the diagnosis and treatment of various forms of cancer, disinfection of blood and its components from pathogenic viruses, as well as as artificial oxygen carriers [16].

One of the main classification features of systems formed by high molecular weight compounds and porphyrins is the method of binding tetrapyrrole macrocycles to the carrier polymer. According to this feature, two large groups of polymer-bound systems are distinguished: physically fixed and chemically bound porphyrins.Porphyrins, which are chemically bound to the polymer, are of particular interest from the point of view of stability of polymer systems, specific properties and variety of applications [17].

EXPERIMENT AND DISCUSSION OF THE RESULTS. Monoaminotetraphenylporphyrin (H_2atpp) was used as a starting porphyrin to obtain a complex with Yb(III) ions, as well as a component of polymeric materials.The synthesis of the complex was carried out according to the improved method in the medium of boiling imidazole, which ensured easier isolation and high yields of the complexes.



Scheme 1 – Structure of studied porphyrins.

The radical polymerization method was used to make samples in the form of films: a solution of porphyrin or metalloporphyrin was prepared in freshly distilled methylmethacrylate with a concentration of 10^{-3} mol/l and 0.01 mol/l of benzoyl peroxide was added. The polymerization process was carried out for 2–3 hours at a temperature of 70–80 °C. Based on measurements of area, density and mass, their thickness was calculated.This technique allowsobtaining films with a thickness from 5 to 1000 μm; films with a thickness of 10 μm were used for spectral analysis.

Attempts to synthesize the Yb-atpp copolymer failed.Complex is demetalated because of the action of benzoyl peroxide, so IR luminescence will no longer be observed in the final material.

Spectra of molecular fluorescence, *4f*-luminescence and excitation spectra were recorded on a spectrofluorimeter "Fluorolog FL 3–22" ("Horiba JobinYvon") using 450 W Xe-lamp. Spectra of 4*f*-luminescence of Yb(III) complexes were registered in 900–1100 nm range (transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$). Spectra of molecular fluorescence of porphyrins were registered at 550–800 nm (S_1-S_0 transitions). Integral intensity of luminescence was measured using software of the device. The relative quantum yield of molecular fluorescence (φ_{ML}) was determined using solution of Zn-tpp (H_2tpp – 5,10,15,20-tetraphenylporphyrin) in ethanol as a primary standard (0.022). Determination of the φ_{ML} (accuracy is ±10%) was made using formula:

$$\Phi_{ML} = \varphi_0 I_x A_0 n_x^2 / (I_0 A_x n_0^2),$$

where φ_0 and φ_x – luminescence quantum yield of the standard and of the sample respectively,
A_0 and A_x – absorption at the wavelength of Soret band of the standard and of the sample respectively,
I_x and I_0 – integral luminescence intensity of the standard and of the sample respectively,
n_0 and n_x – refractive index of the standard medium and of the sample medium respectively.

Technologies for producing materials, which can emit in a given range and given intensity or capable of transforming light from one range to another, require polymer matrices of high strength and photostability. An important aspect is that almost all technologies require the optical transparency of the final polymer product. The absence of color is achieved by the introduction of modifiers for some polymers, but, for example, the polymethyl methacrylate (PMMA)homopolymer retains optical transparency in the visible and part of the UV and IR ranges of light without the addition of any components, so it is an interesting model polymer matrix for the construction of photoactive materials.

PMMA, polystyrene (PS) and a copolymer of PS with PMMA in the molar ratio of 0.25/0.75, 0.5/0.5 and 0.75/0.25 were studied as polymer matrices in the work for the manufacture of thin films with a thickness of 10 μm.

Thin-layer films for the study of porphyrin-sensitized *4f*-luminescence in a polymer matrix were obtained from PMMA containing such porphyrin derivatives as: 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin and its complex with the Yb(III) ion (acetylacetonate in as an axial ligand).

The most interesting results were obtained on PMMA films, and the advantages of this material can be highlighted as follows: 1. Resistance to UV radiation and high transmittance: PMMA polymer has a high light transmittance (92%), which exceeds the indicators of other polymer materials. Its resistance to UV radiation

makes it effective for applications exposed to solar radiation. 2. Filtration of hard ultraviolet light: Polymethyl methacrylate does not transmit ultraviolet light at wavelengths below 300 nm, similar to ordinary glass. 3. Infrared light: Polymethyl methacrylate transmits infrared light up to 2,800 nm and blocks longer wavelength infrared light up to 25,000 nm, making it excellent for applications involving near-IR radiation zones. 4. Wide application: Compared to materials like polystyrene and polyethylene, PMMA is widely used for outdoor applications due to its optical properties and resistance to environmental influences.

Copolymers

The given properties of the obtained modified films are especially valuable considering the fact that porphyrins are very stable macrocyclic compounds due to the 18π-aromatic system, which is a strong argument for obtaining materials with excellent operational characteristics and shelf life. In addition, due to high molar absorption coefficients, the required concentration of porphyrins in the starting material is extremely low, which ensures its availability. Note, that the nature of the matrix and the method of preparation affect the emission characteristics, as can be seen from the data in the Table 1. For example, the samples of lanthanide-porphyrin copolymersfilms actually do not contain Yb complexes, instead they are only porphyrin-containing because of demetalation (control of UV-vis absorption spectra) and their characteristics are almost the same as for the corresponding materials with H_2atpp.

The properties of materials H_2atpp-PMMA, H_2atpp-PS and copolymer materials **1** (PMMA/PS = 0.25/0.75), **2** (PMMA/PS = 0.5/0.5), **3** (PMMA/PS= 0.75/0.25) are shown in Table 1. Note, that the final materials, which obtained under copolymerization conditions are not perfectly transparent, therefore, unlike solutions, the absorption spectrum of the final material cannot be recorded with good resolution and its observable profile actually consists of the two most intense bands with maxima at approximately 420 nm (Soret band) and 516 nm (fourth *Q*-band).

Table 1.

Photophysical parameters of copolymer materials (298 K, C=1×10^{-5}M).

Compound	λ_{abs}, nm	λ_F, nm	E_{S1},cm^{-1}	$\varphi_F \times 10^{2*}$
H_2atpp-PS	420,516	654	15290	6
1	420,514	655	15270	7
2	419,514	653	15310	7
3	419,514	653,720	15310	7
H_2atpp-PMMA	419,514	653,718	15310	8
Yb-atpp-PS	420,516	–	15290	6
Yb-1	420,514	–	15270	8
Yb-2	419,514	–	15310	8
Yb-3	419,514	–	15310	10
Yb-atpp-PMMA	419,514	–	15310	11

* ± 10%

For porphyrin-containing films, the ratio of intensities of both bands of molecular fluorescence (MF) in the spectrum profile is preserved despite the variability of the composition of PS and PMMA in the copolymer. Also, which is very important, a weak hyperchromic shift of both MF bands is observed when the PMMA component increases. The increase in the quantum yield in the sequence **1**<**2**<**3** can be explained by a higher light transmission coefficient for PMMA compared to PS.

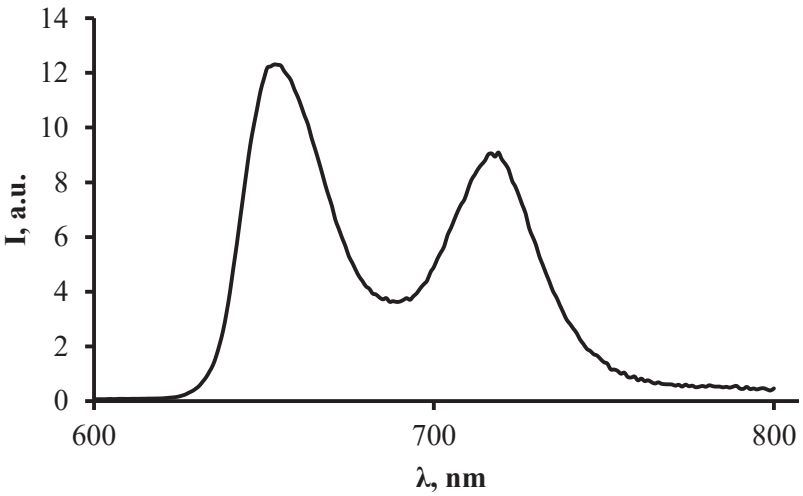


Fig. 1 – Fluorescence spectrum of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrinin a film based on PMMA.

The positions of maxima at 653 and 718 nm in the molecular fluorescence spectra of films containing H_2atpp (Fig. 1) correspond to the spectra of porphyrin solutions. Thus, the use of porphyrin compounds with unquenched fluorescence makes it possible to transform the light of the near UV and blue visible region into red light.

Doped polymers

Absorption spectra of porphyrin-containing materials H_2atpp-PMMA, H_2atpp-PS and mixed-polymer materials **4** (PMMA/PS = 0.25/0.75), **5** (PMMA/PS = 0.5/0.5), **6** (PMMA/PS = 0.75/0.25) and their lanthanide-porphyrin analogsare shown in Table 2. In contrast to copolymerization, the films obtained by coprecipitation are formed transparent, which allows obtaining an absorption spectrum with good resolution. Its profile fits with the spectrum of the DMF solution and consists of five bands with maxima at approximately 420 nm (Soret band), 514, 551, 593, and 648 nm (visible region *Q*-bands).

Similar to absorption spectra, fluorescence spectra of porphyrin-containing materials also have a clear spectrum with characteristic bands at 650 and 720 nm. The higher fluorescence efficiency of the obtained samples, in comparison with their copolymer analogues, is due to the quality of the film, which minimally scatters both the photoexcitation light and the porphyrin fluorescence arising in the material (Table 2). The tendency of increasing the fluorescence quantum yield as the PMMA content increases remains similar to the materials obtained by the first method, which, in our opinion, is also related to the degree of transparency, which is directly proportional to the quantum yield value.

Table 2.

Photophysical parameters of doped polymer materials obtained by coprecipitation (298K, C=1×10^{-5}M).

#	λ_{abs}, nm	λ_{max}, nm		E_{S1}, см$^{-1}$	φ×10^{2*}	
		MF	*4f*		MF	*4f*-lum
H_2atpp-PS	419,514,551,593,648	654,720	–	15290	9	–
4	419,514,551,593,648	655,721	–	15270	9	–
5	419,514,551,593,648	653,719	–	15310	10	–
6	419,514,551,593,648	653,720	–	15310	11	–
H_2atpp-PMMA	419,514,551,593,648	653,718	–	15310	12	–
Yb-atpp-PS	426,557,593	–	980	–	–	2.1
Yb-4	427,558,594	–	980	–	–	2.1
Yb-5	427,558,594	–	978	–	–	2.2
Yb-6	427,558,594	–	978	–	–	2.1
Yb-atpp-PMMA	427,558,594	–	978	–	–	2.3

* ± 10%;

It is known that in the solid state the fluorescence of porphyrins is very weak compared to solutions. This is explained by concentration quenching. It consists in the fact that the first intense emission band of porphyrin with a maximum at 650 nm almost perfectly coincides with the last absorption band with a maximum at approximately the same 650 nm. Due to the large value of the molar extinction coefficient (lgε>4) of the specified absorption band, neighboring tetrapyrrole molecules effectively absorb the emitted light, and this chain process, combined with energy dissipation at each step, leads to extremely low quantum yield values. But in the case of the proposed materials, the concentration was selected in such a way that the effect of concentration quenching was minimal with sufficient radiation efficiency.

Porphyrin-sensitized *4f*-luminescence of the Yb(III) ion at 978 nm (transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$) was recorded in polymer matrices of various nature (Fig. 2).

It is observed that the quantum yield valuesof *4f*-luminescence in ytterbium-containing materials does not depend on the type of polymer matrix and the variability of its composition (Table 2). An important argument in explaining such a phenomenon is almost 100% transparency of the studied polymers in the area of ytterbium ion radiation (980 nm) compared to its approximately 90% transparency for the visible range, so in contrast to the latterthe quantum yield of NIR-luminescence ofytterbiumshould be less sensitive to the type of polymer. Another important factor is the peculiarity of the IR light itself, which consists in the almost complete absence of light scattering compared to the visible and UV ranges. That is, IR light is more stable in such materials in contrast to visible light, and its efficiency remains under any conditions that were studied.

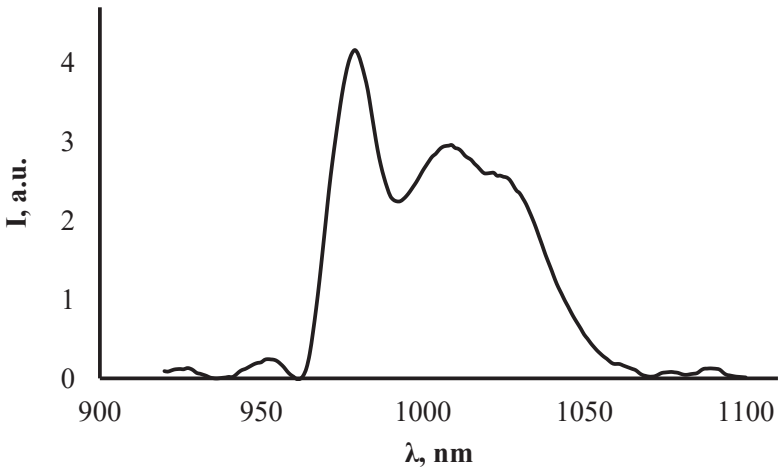


Fig. 2 – *4f*-Luminescence spectrum of the Yb(III) ion in a PMMA-based film doped with a complex in the IR region.

Thus, it was established that the Yb(III) complex with 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin is a modifier of PMMA, to give it the ability to transform visible light into IR light, due to the 4f-sensitizing activity of the porphyrin.

It is also important that the first samples of the obtained films do not change their optical characteristics during one year from the moment of their formation. Fig. 3 showsstable both molecular fluorescence and *4f*-luminescence efficiency (within equipment error).

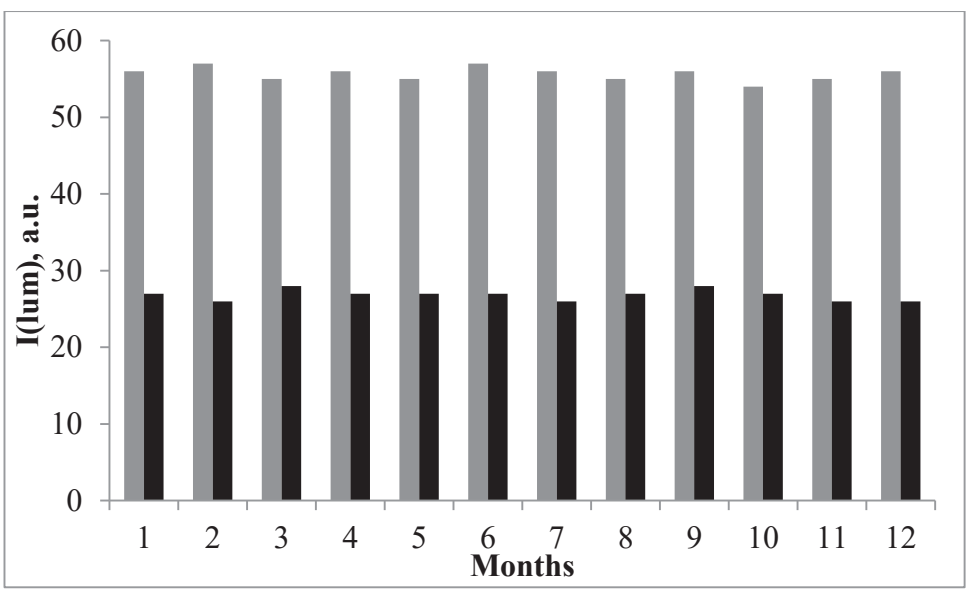


Fig. 3 – Changes in the intensity of different types of emission of PMMA-based materials (H_2atpp-PMMA – fluorescence, grey color; Yb-atpp-PMMA – IR-luminescence, black color) over the course of a year.

This effect can be explained by the extraordinary stability of PMMA even to UV radiation and the high stability of porphyrin molecules. On the other hand, lanthanide porphyrins are relatively labile structures and can be easily demetalated under the action of many components of air or liquids that may contact with them. This applies, for example, to solutions or compounds in their pure form, however, in this case, complexes that are completely surrounded by a polymer have no possibility of interaction with the external environment. This does not apply to molecules located on the surface of the material, but their number compared to others in the material is extremely small, so even the absorption spectrum does not change in any way with the appearance of demetalated compounds on the surface.

CONCLUSIONS. It is shown that Yb-centered IR emission in PMMA-, PS-based films is much less susceptible to changes in the chemical composition of the material base than fluorescence in the visible range. It was also demonstrated not only the preservation of the mechanical stability of the materials over a long period of time, but also their emission parameters. In particular, when using a low concentration of lanthanide-porphyrin of 0.1% in the final material, the efficiency of the infrared emission of the Yb(III) ion remains at the level of the corresponding methanol solution.

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ВИПРОМІНЮВАННЯ У ВИДИМІЙ ТА БЛИЖНІЙ ІНФРАЧЕРВОНІЙ ОБЛАСТІ ПОЛІМЕРНИХ МАТЕРІАЛІВ, ЩО МІСТЯТЬ ПОРФІРИН ТА ЙОГО ПОХІДНУ ІТЕРБІЮ

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Отримано серію порфіриновмісних полімерних матеріалів різної структури. На основі 5-(*n*-амінофеніл)-10,15,20-трифенілпорфірину та його ітербієвої похідної одержано матеріали різної будови, які отримано за різних підходів. Для всіх отриманих матеріалів характерна люмінесценція – вони випромінюють у видимому або ближньому інфрачервоному (ІЧ) діапазоні. З'ясовано, що ІЧ-випромінювання є значно менш чутливим до змін хімічного складу полімерної основи, ніж флуоресценція у видимому діапазоні. Також було показано, що отримані матеріали є стабільними та зберігають свої емісійні параметри протягом тривалого часу. Використання низької концентрації (0,1%) ітербій-порфірину в кінцевому матеріалі дозволяє залишати ефективність інфрачервоного випромінювання іона Yb(III)

на тому ж рівні, що й у відповідному розчині метанолу.

Ключові слова: полімери, лантаноїди, порфірини, флуоресценція, 4*f*-люмінесценція.

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