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White emission of polymeric luminescent compositions doped with boron chelates

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Multicomponent polymeric luminescent compositions doped with β-diketonates of boron difluoride were obtained, which can be used to produce white light by cascade radiative energy transfer. The white light is obtained by using the RGB model. The compositions containing four luminophores showed high color rendering values (color rendering index > 80, 2776 K). Two luminescent transitions were realized in the obtained compositions for the red dye (R): $S_1 \rightarrow S_0$, associated with cascade radiative energy transfer along the chain of luminophores, and $S_2 \rightarrow S_1 \rightarrow S_0$, directly excited by UV radiation. The luminous characteristics of the obtained compositions indicate the possibility of using polymeric luminescent compositions doped with β-diketonate boron difluoride in emergency and indoor lighting devices.

Keywords: β-diketonates of boron difluoride, luminescence, polymer compositions, energy transfer, white light, illumination.

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Introduction

With the development of science and technology, there is a growing need for mankind to use artificial lighting. At the same time, light devices must have a number of characteristics: energy efficiency, high color rendering, a certain correlated color temperature (T_{textCT}), resistance to external influences, low cost, long service life, a certain spectral composition [1]. The latter is most important in interior lighting systems. For the human eye, sunlight is most suitable, therefore, the most favorable light source for humans will be a source of light with a spectral distribution close to the sun radiation.

Incandescent, luminescent lamps, and white LEDs can be used for artificial lighting systems. Among commercially available sources of light, incandescent lamps have the closest spectrum of radiation to sunlight, but the low efficiency of these light sources limits their use. Fluorescent lamps have an irregular, linear spectrum and are characterized by pulsations [2], which has a negative effect on human health. White LEDs offer high efficiency, fast performance, accurate light directionality, low operating voltage, shock resistance and low maintenance costs. There are a number of ways to produce white light with LEDs [3]: combining blue, green and red LEDs, combining blue and yellow LEDs, mixing blue LED emission with yellow luminophore emission, mixing UV LED emission with blue, green and red luminophore light, mixing UV LED emission with blue and yellow luminophore light. To obtain white LED emission, it is necessary to select the current values corresponding to the maximum quantum yield of emission for each crystal. Applying a layer of luminophores to UV or blue LED crystals is currently the simpler and more cost-effective way to produce white light [3].

The main disadvantage of LED light sources is the high initial cost relative to incandescent and luminescent lamps, which is associated, among other things, with the use of a large number of LED crystals due to the fundamental limitation of the external quantum efficiency value. The solution to this problem could be the use of laser diodes [4].

Another problem is related to the fact that in the emission spectrum of traditional white light-emitting diodes bright blue component (440–460 nm), emitted by the crystal itself (in blue LEDs) or luminophore (in UV LEDs), on which the human eye focuses on objects worse than the green color (about 555 nm). This leads to a rather low color rendering index (CRI). In this case, in accordance with the regulatory requirements for general and local lighting of the premises light sources with T_{CT} from 2400 to 6800 K should be used. The CRI of LED light sources must be at least 80 for indoor lighting, at least 40 [5] for emergency lighting, at least 70 [6] for luminaires used for outdoor utility lighting and industrial workplace lighting with no color rendering requirements. As a result, the emission spectrum of such white LEDs contributes to the generation of a blurred image on the human retina, which leads to reduced performance and increased fatigue, and can also lead to photochemical damage to the retina [7].

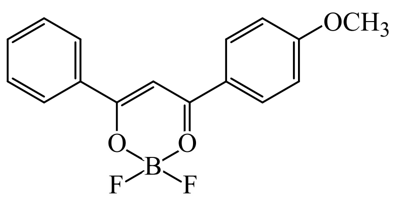
The emission layer applied to the LED crystal is usually polymer luminescent compositions (PLCs) doped with yttrium-aluminum garnet-based compounds [4]. These compounds provide satisfactory spectral characteristics, but are characterized by the presence in the composition of rare earth elements, which negatively affects the cost of both the PLC itself and the LED light source.

The use of new emission materials in the design of white LEDs can potentially reduce the blue component in the resulting spectrum and bring it closer to natural light without increasing the cost of the final product. New substances of both inorganic [8,9] and organic [10,11] nature are proposed for these purposes.

One alternative is PLCs doped with β-diketonates of boron difluoride. Distinctive features of this compound class representatives are the formation of *J*-aggregates in saturated solutions and highly concentrated PLCs, which leads to an increase in photostability [12]. In addition, β-diketonates of boron difluoride are notable for their easy preparation [13], high quantum yield of luminescence solutions and crystals in the entire visible and near-infrared range. It was noted that excimer luminescence in saturated solutions and crystals of β-diketonates of boron difluoride allows obtaining different color combinations using a single luminophore. In particular, the use of a saturated solution of dibenzoylmethanate of boron difluoride promotes white emission due to the presence of broad bands of monomer and excimer luminescence [14].

Earlier, we showed that boron dibenzoylmethanate in polystyrene (PS)-based PLCs forms exciplexes with the phenyl rings of the polymer [15]. The introduction of boron difluoride anthra-cenoicetonate into this composition leads to the realization of effective radiative energy transfer with the formation of the resulting white radiation [16]. However, a dye (boron difluoride anthra-cenoicetonate) with a low quantum yield of fluorescence was used as an acceptor.

In this work, multicomponent light-transforming PLCs based on PS doped with β-diketonates of boron difluoride that emit white light as a result of the simultaneous realization of different pathways of radiative energy transfer were obtained and investigated. The white light is obtained by using the RGB model. Compounds **1**, **2**, **3**, **4**, and **5** (scheme) with high quantum yield of luminescence were chosen as luminophores. The luminescence bands of this series of compounds cover the entire area of the visible wavelength range. The luminophores **4** and **5** were used to produce red (R) radiation, **3** — green (G), **1** and **2** — blue (B).



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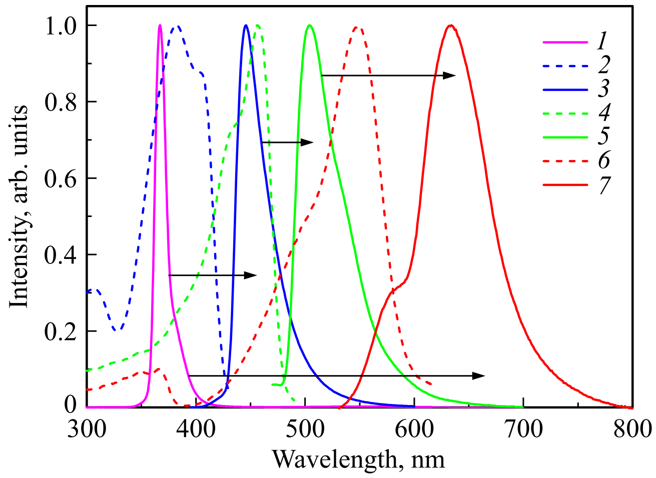
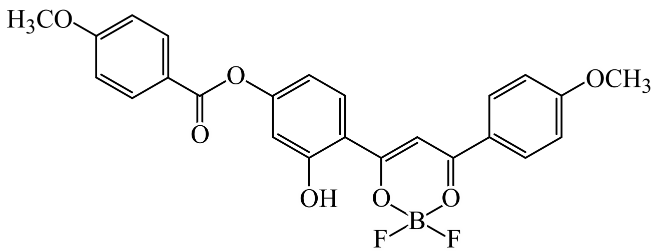


Figure 1. UV source spectrum (*1*) and normalized luminescence excitation (dashed lines) and luminescence spectra (solid lines) of PS films with 0.2% **1**(*2,3*), **3** (*4,5*) and **4** (*6,7*).



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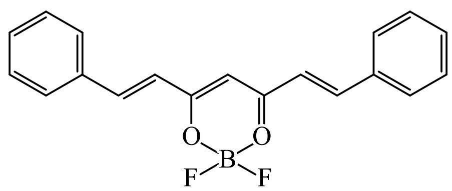

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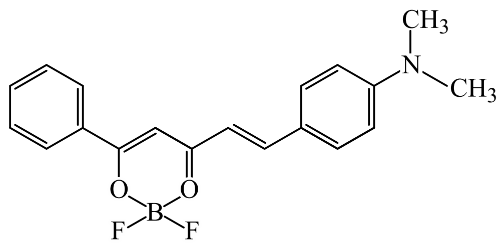

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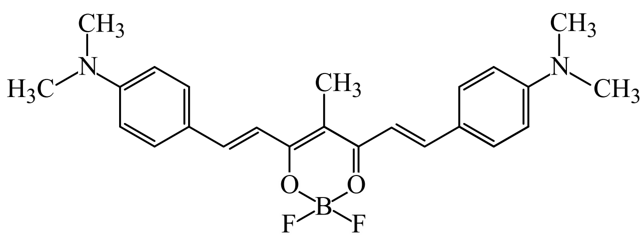

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Table 1. Spectral characteristics of PS-based PLCs doped with 0.2% **1**, **2**, **3**, **4** and **5**

Dye	λ_{abs}, nm	λ_{lum}, nm	FWHM**, nm	Color
1	398	446	33	B
2	410	479	41	B
3	342	504	49	G
4	370, 524	580, 604*	70	R
5	588	631, 656*	103	R

Note. * The luminescence bands of the dye aggregates. ** Width at half-height level (FWHM).

Materials and methods

The initial β-diketonates of boron difluoride were obtained and purified according to the works: **1** [17], **2** [18], **3** [19], **4** and **5** [20]. Hexane, dichloromethane, and 1,2-dichloroethane (ECOS-1) were used without additional purification. PS of PSM-115 grade (NevaReactiv), purified by hexane resuspension from dichloromethane solution, was used as a polymer matrix.

Luminescence spectra were recorded on a Shimadzu RF5301 spectrofluorimeter using „Panorama 3.4"software. 365 and 380 nm bands corresponding to the emission of commercially available UV LEDs were chosen as the excitation radiation. Chromaticity coordinates (CIE 1931) and color rendering coefficients were calculated using ColorCalculator 6.75 software.

Solutions for PLC production were made by dissolving PS and precise proportions of luminophores from 0.01 to 0.15% of the polymer weight in 1,2-dichloroethane. The films were formed by solution pouring. The solution was applied dropwise to the cleaned glass surface and dried in a fume hood for 24 h at room temperature. The obtained films were separated from the substrate under a layer of distilled water.

Results and discussion

The luminescence and luminescence excitation maxima **1, 2** and **3** in PS correspond to the dye bands in [18,19,21] solutions (Table 1). In the luminescence spectrum of dye **4** in the PS matrix (Fig. 1), a short-wave shoulder (580 nm) corresponding to monomeric luminescence and a long-wave maximum (604 nm) corresponding to luminescence of aggregates, whose formation is typical at high concentrations of luminophore in the polymer [22] are observed. In addition, dye **4** in the PS matrix, as in the solutions, is characterized by the presence of two luminescent transitions: an intense band in the red-orange area (transition $S_1 \rightarrow S_0$) and short-wave luminescence in the blue area (transition $S_2 \rightarrow S_0$) [20]. Thus, in the PLC based on **4**, two ways of luminophore excitation are realized (Fig. 1): excitation through cascade energy transfer through the chain of luminophores **1-3-4** (transition $S_0 \rightarrow S_1$ — 524 nm) and

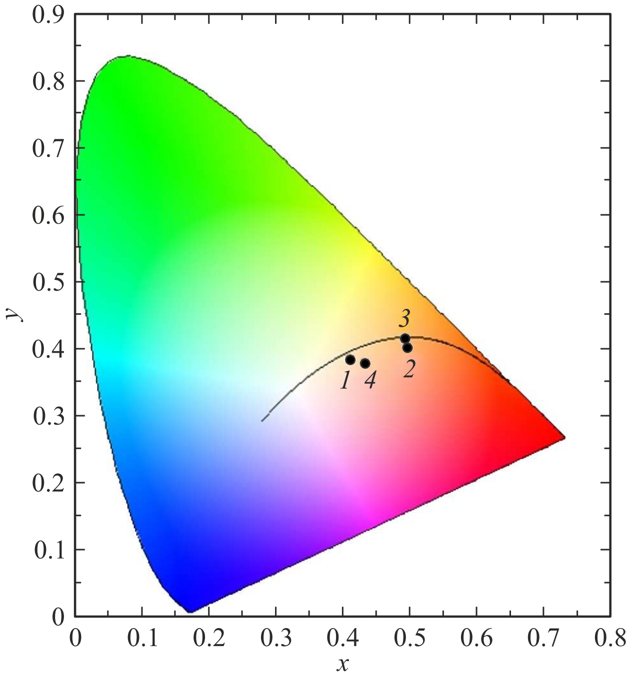

Figure 2. CIE 1931 color space with PLC chromaticity coordinates I (*1*), II (*2*), III (*3*) and IV (*4*) at excitation wavelength of 365 nm.

excitation directly by UV radiation (transition $S_0 \rightarrow S_2$ — 370 nm). For dye **5** in the PS matrix (Table 1), in addition to the monomeric fluorescence (631 nm), the presence of brightly luminescent aggregates (656 nm) [22] is also observed.

Dye **1** is characterized by the shortest wavelength luminescence of 446 nm (Fig. 1, Table 1), the band of which is close to the emission maximum of commercially available blue light-emitting diodes (450 nm). For **1**, the full width at half-height level (FWHM) has the lowest value (33 nm) among the β-diketonates of boron difluoride studied in this work (Table 1). The luminescence spectrum of dye **2** compared to **1** is characterized by a wider band (FWHM = 41,nm, Table 1), capturing the blue and green areas of the visible spectrum, which makes it possible to obtain compositions that emit white light based on the two-dye system **2-4** (PLC I). In order to obtain the resulting white emission in the present work, PLCs with a combination of three luminophores **1-3-4** (PLC II and PLC III, differing in the ratio of dyes) were also fabricated. The compositions were chosen so that the donor and acceptor luminescence bands overlapped to realize cascade radiative energy transfer (Fig. 1).

Based on the luminescence spectra of the obtained PLCs at excitation wavelengths of 365 or 380 nm, corresponding to commercially available UV LEDs, we calculated the color space chromaticity coordinates of the International Commission on Illumination (CIE) 1931 T_{CT}, CRI, total color rendering index on the color quality scale (Qa) (Table 2). The obtained PLCs are characterized by a

Table 2. Color characteristics of the received PLCs

PLC	Composition of composition	Molar ratio	λ_{UV^*}, nm	Coordinates of CIE chromaticity 1931		T_{CT}, K	CRI	Qa
				x	y			
I	**2-4**	3 : 1	365 380	0.41 0.37	0.38 0.35	3287 3963	58 63	56 57
II	**1-3-4**	2 : 2 : 1	365 380	0.50 0.48	0.40 0.40	2203 2312	58 60	60 60
III	**1-3-4**	3 : 2 : 1	365 380	0.49 0.48	0.41 0.41	2314 2457	60 61	64 65
IV	**1-3-4-5**	1:3:0.6:0.4	365 380	0.44 0.42	0.38 0.37	2776 027	90 85	96 95

* The emission band of the excitation source of UV radiation.

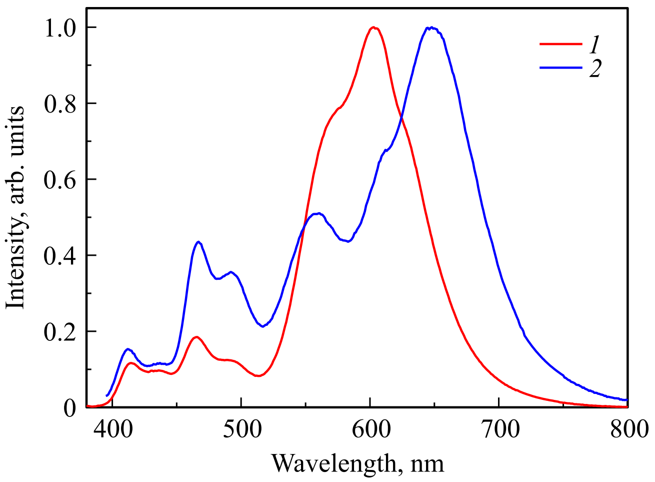

Figure 3. Luminescence spectra of PLC III ($\lambda_{exc} = 365$ nm) (*1*) and IV ($\lambda_{exc} = 365$ nm) (*2*).

white glow, the chromaticity coordinates on the CIE 1931 color space are located near the emission line of an absolutely black body (Fig. 2). However, for PLCs I-III unsatisfactory color rendering is observed, which is associated with the absence in the spectrum of the long-wave leaving 700–780 nm (Fig. 3). In addition, for these PLCs, a high-intensity luminescent dye **4** band in the red area (604 nm) is observed, which is due to the simultaneous realization of two excitation pathways (Fig. 1) associated with cascading radiative energy transfer in the **1-3-4** series (transition $S_0 \rightarrow S_1$ — 524 nm, radiative transition $S_1 \rightarrow S_0$ — 580 and 604 nm) and by excitation directly by UV radiation $S_0 \rightarrow S_2$ — 370 nm, radiative transition $S_2 \rightarrow S_1 \rightarrow S_0$ — 580 and 604 nm). This accounts for the low T_{CT} and the shift of the CIE chromaticity coordinates to the red-orange area (Fig. 2, Table 2).

In order to broaden the emission spectrum, a four-dye **1-3-4-5**-based PLC (PLC IV) was fabricated to which a symmetrical dimethylaminostyryl β-diketonate of boron difluoride **5** with long-wave luminescence in the red area was added (Table 1). This allowed to extend the emission spectrum of PLC IV into the red area in the 700-780 nm range (Fig. 3, *b*) compared to PLC III and achieve high CRI and Qa values (Table 2) both when excited by 365 nm and 380 nm emission. This potentially allows the PLC IV to be used for lighting purposes, in particular for residential lighting.

Conclusions

In two, three, and four-component polymeric luminescent compositions doped with β-diketonates of boron difluoride, in which the dyes are selected so that the donor luminescence band overlaps with the acceptor luminescence excitation band, a cascade radiation energy transfer is realized upon irradiation with UV radiation, contributing to the resulting white light. The combination of two and three luminophores in one composition with UV radiation contributed to obtaining radiation with color characteristics suitable for emergency lighting (CRI> 40). For the four-component composition, white light was obtained with color characteristics satisfying the values required for indoor lighting sources (CRI > 80, 2776 K). The low correlated color temperature is due to the presence of an intense luminescence band in the long-wave area due to the simultaneous realization of two luminescent red dye transitions ($S_1 \rightarrow S_0$ and $S_2 \rightarrow S_1 \rightarrow S_0$) related to the cascade radiative energy transfer and luminescence excitation directly by UV radiation. Further study of representatives of this class of substances as light-transforming materials is promising.

Conflict of interest

The authors declare that they have no conflict of interest.

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