Polymeric Luminescent Compositions Doped with Beta-Diketonates Boron Difluoride as Material for Luminescent Solar Concentrator

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Abstract. In this paper we investigated polymeric luminescent compositions based on polystyrene doped with beta diketonates boron difluoride. Transparent films with effective absorption in the ultraviolet and blue regions of the spectrum were obtained. Polymeric luminescent compositions based on the mixture of dyes allow expanding the absorption region and increase the radiation shift. A luminescent solar concentrator consisting of a glass plate coated with such film can be used for photovoltaic window application.

1. Introduction

Windows are an important component of buildings, because they perform various necessary functions [1]. First of all, windows are an important part of the urban design. 60 % of surface area of a standard skyscraper is covered with glass [2]. This allows getting attractive appearance of buildings and reduces lighting costs, because, secondly, windows are an important source of daylight [3-5]. Thirdly, windows have a significant effect on heating/cooling of buildings [6,7].

Various groups of researchers are working to reduce energy consumption through optimization of window parameters [4,6,7] and integration of smart windows into buildings [3]. Another way to reduce energy consumption is the use of glazing systems, which are capable to generate energy.

Luminescent solar concentrator (LSC) consists of transparent lightguide doped with luminescent dye, which selectively absorbs part of the incident sunlight and re-emits this light at a longer wavelength range due to the Stokes shift. A fraction of the re-emitted light escapes through the loss cone, but the main part is concentrated at edges of the plate due to the total internal reflection. Photovoltaic (PV) cells are mounted on the edges and absorb radiation, which is converted into electricity [8,9]. LSC can be used in various ways such as integration into greenhouses [10], building facades [11], but PV window is one of the most perspective applications [12].

The external quantum efficiency (EQE), defined as the ratio of the number of electron–hole pairs generated to the number of photons incident on the front surface of the cell, for most PV cells has a low value at shortwave range and reaches an acceptable value at 500 nm and higher [13]. Therefore many researchers use red luminescent dyes [14-16]. However, LSC based on red dyes is characterized by low absorption in the shortwave range, therefore ultraviolet (UV) and blue regions of sunlight are
used to a small extent. Moreover, a room with full red glass windows is not comfortable for people [2]. LSCs based on red dyes can be used as canopies in modern buildings [16], but not for existing edifices in such application. Transparent colorless LSC [17] for PV window application is more comfortable for people, because it is indistinguishable from usual window glass.

The Stokes shift is a parameter that has a significant influence on the efficiency of LSC. An increase of this parameter results in an increase of the maximum size of LSC at which sufficient efficiency is achieved [17]. It is very important when it is necessary to obtain a large size LSC for PV window application. Thus, it is necessary to obtain a transparent colorless lightguide based on dye with a significant Stokes shift and high absorption intensity in the UV and blue region of the spectrum for LSC application.

Boron difluoride dibenzoylmethanate (BF$_2$DBM) is useful for this purpose. Figure 1 shows that the dye has a light yellow color in the crystalline state, but it allows obtaining colorless solutions in organic liquids and polymeric luminescent compositions (PLC). Moreover, BF$_2$DBM belongs to $\beta$-diketonates boron difluoride. The distinctive feature of this class of compounds is the ability to form excimers, which increase the photostability of the dye [18]. In this work we demonstrate the possibility of using of PLCs doped with $\beta$-diketonates boron difluoride for LSC application.

![Figure 1: Photograph of crystalline BF$_2$DBM. (b) Photograph of the transparent polymeric film doped with BF$_2$DBM.](image)

**Figure 1.** (a) Photograph of crystalline BF$_2$DBM. (b) Photograph of the transparent polymeric film doped with BF$_2$DBM.

2. Experiment

In the present study, polystyrene (PS) films doped with BF$_2$DBM (concentrations are 0.2, 0.4, 0.6, 0.8 and 1 wt. %; thickness is 0.1 mm), boron difluoride anthracenoylacetonate (AntAcBF$_2$) (concentration is 0.2 wt. %; thickness 0.03 mm) and mixture of AntAcBF$_2$ and BF$_2$DBM (AntAcBF$_2$ concentration is 0.2 wt. %; molar ratio AntAcBF$_2$ to BF$_2$DBM is 1:1; thickness is 0.03 mm) were fabricated by the pouring method of PS (1 g) solution in toluene (20 ml). Figure 2 shows the molecular structures of luminophores. Films are shown in figure 3.

![Figure 2: Molecular structures of BF$_2$DBM (a) and AntAcBF$_2$ (b).](image)

**Figure 2.** Molecular structures of BF$_2$DBM (a) and AntAcBF$_2$ (b).
Figure 3. Photographs of PS films doped with BF$_2$DBM (a), (d), AntAcBF$_2$ (b), (e) and mixture of BF$_2$DBM and AntAcBF$_2$ (c), (f) under normal conditions and shortwave ($\lambda = 365$ nm) radiation, respectively.

Luminescence and excitation spectra of films were recorded on a spectrofluorimeter Shimadzu RF5301. Light-emitting diode (LED) Cree UV 365 nm was used to irradiate films by shortwave radiation. Transmittance spectra of LED radiation were registered by spectrometer Ocean Optics Maya 2000 Pro.

3. Results and discussion
The spectral distribution of the sunlight in figure 4 has a significant UV fraction (<400 nm), which corresponds to the maximal excitation of PS film doped with BF$_2$DBM in figure 5. Irradiation of film leads to a shift of shortwave radiation to a blue region of spectrum (430 nm). Transmittance spectra in figure 6 show that film with a thickness of 0.1 mm and a BF$_2$DBM concentration of 0.4 wt. % and more is enough for the complete shift of even high-intensity UV radiation of LED to a longer wavelength blue region of the spectrum. This fact indicates that these PLCs can be used for LSC application.

Figure 4. Normalized emission ($\lambda_{\text{exc}} = 380$ nm) and excitation ($\lambda_{\text{em}} = 515$ nm) spectra of a mixture of AntAcBF$_2$ and BF$_2$DBM, along with the AM1.5G solar spectrum [19].

Figure 5. Normalized emission and excitation spectra of films doped with BF$_2$DBM ($\lambda_{\text{exc}} = 380$ nm, $\lambda_{\text{em}} = 430$ nm) and AntAcBF$_2$ ($\lambda_{\text{exc}} = 435$ nm, $\lambda_{\text{em}} = 515$ nm).
Figure 6. Transmittance spectra of the UV LED through films doped with BF$_2$DBM with a thickness of 0.1 mm.

Figure 7. Photographs of LSCs based on glass plate covered with films doped with BF$_2$DBM (left) and AntAcBF$_2$ (right) under normal conditions (a); under shortwave ($\lambda = 365$ nm) radiation (b).

Fabrication of LSC based on polymeric material with a sufficient thickness for mounting of PV cells at edges is not the optimal decision. LSC can be fabricated by coating a glass plate with a PLC [20]. In this case, both the film and the glass work as a single LSC and the re-emitted light is concentrated at edges. The total absorption of the UV fraction of sunlight can be controlled by two parameters such as thickness of film and concentration of BF$_2$DBM. In the case of BF$_2$DBM using this way allows obtaining colorless LSC. LSCs based on glass coated with PLCs are shown in figure 7.

The range of BF$_2$DBM emission still corresponds to low EQE of PV cells [13]. Moreover, LSCs, which absorb the light at UV-region of spectrum, are ultimately limited to efficiencies lower than 5% due to the limited UV fraction in the solar spectrum [17]. In addition, the Stokes shift of BF$_2$DBM is only 42 nm and potentially does not make it possible to obtain an effective large-area LSC due to loss of self-absorption. Using a mixture of dyes makes it possible to expand the absorption region of a PLC [21] by energy transfer from one dye to another [22].

In order to shift the UV radiation at longer wavelength and to expand the absorption region of the PLC based on BF$_2$DBM and thereby increase the LSC efficiency, it is necessary to add one more dye, which excitation maximum coincides with the BF$_2$DBM emission. AntAcBF$_2$ is suitable for this purpose. In this case, radiative energy transfer from BF$_2$DBM (donor) to AntAcBF$_2$ (acceptor) is realized [23]. Moreover, the Stokes shift of AntAcBF$_2$ is 74 nm, which is larger than that of BF$_2$DBM. The overlapping of the AntAcBF$_2$ excitation spectrum and the BF$_2$DBM luminescence spectrum in PS films is shown in figure 5.

Excitation spectrum of film doped with mixture of BF$_2$DBM and AntAcBF$_2$ is shown in figure 4. The mixture provides more uniform excitation of dyes at the UV and blue spectral ranges in contrast.
to individual luminophores. Luminescence band of BF$_2$DBM has low intensity due to absorption by the excitation band of AntAcBF$_2$. The radiative energy transfer shifts the radiation from the UV to the yellow-green region of the spectrum, which corresponds to an acceptable value of EQE for most PV cells [13]. AntAcBF$_2$ does not allow obtaining a colorless film, but LSC based on glass coated with such PLC, which is shown in figure 7, has a faint colored tinting.

4. Conclusion
We have studied PLCs based on PS doped with BF$_2$DBM, AntAcBF$_2$ and their mixture. BF$_2$DBM allows obtaining transparent colorless PLCs with effective absorption of radiation in the UV range. The addition of AntAcBF$_2$ allows expanding the absorption region and shift the UV radiation to the yellow-green spectral range in which the EQE of PV cells is higher. The investigated PLCs allow obtaining transparent faint tinted LSCs consisting of a glass plate coated with a polymeric film, which can be used for PV window application.

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