Electroluminescence and photosensitivity spectra of organic diode structures based on zinc complexes

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Abstract. Devices based on zinc complexes with sulphanylaminosubstituted ligands are characterized by dual function – electroluminescence (EL) and photosensitivity. Both EL and photosensitivity are associated with the formation of exciplexes.

The zinc complexes with sulfanilaminosubstituted ligands are shown to be the efficient electroluminescent materials [1]. Light-emitting diodes (OLEDs) based on these complexes are characterized by long-wavelength emission bands that are associated with the formation of exiplexes (excited complexes) between the molecules of the emitting material (zinc complex) and hole-transport material included in the structure of the OLED [1,2]. At the same time, the formation of exciplex can result in photosensitivity of the diode structure, since exciplex is a complex with charge transfer and may arise under photoexcitation. Further charge separation under the action of an external electric field may lead to the appearance of photocurrent. Here we study photosensitivity properties of the diode structures described in ref. [1,2] as OLEDs. Figure 1 show the examples of the electroluminescence (EL) spectra and photocurrent curves (under illumination AM1.5) for the same diode structures of this type.

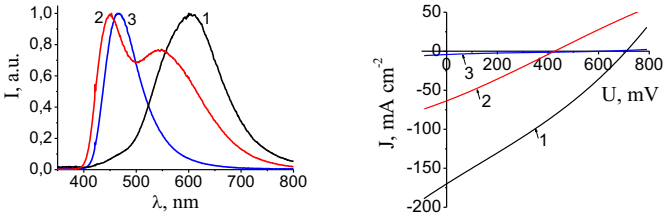

Fig. 1. The EL spectra (a) and the photocurrent curves (b) for the diode structures: (1) ITO/PTA/Zn(TSA-BTZ)$_2$/Al:Ca, (2) ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca and (3) ITO/PTA/CBP/Zn(TSA-BTZ)$_2$/Al:Ca.

The efficiency of the exciplex formation depends on the material of the hole-transporting layer contacting with the zinc complex. In the EL spectra, this dependence manifest itself in the ratio of the intensities of the intrinsic radiation band of the zinc complex in the region of 450 nm and the exciplex radiation band in the region of 550 –

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600 nm (Figure 1a). The efficiency of the exciplex formation is reduced in the series of the hole-transporting msterials PTA-NPD-CBP. Only exciplex band at 600 nm, both the intrinsic band at 450 nm and the exciplex band at 545 nm and only intrinsic band at 465 nm are observed correspondingly for PTA, NPD and CBP contacting with the zinc complex. In case of photosensitivity curves, the photocurrent is reduced in the same series PTA-NPD-CBP in accordance with the efficiency of the exciplex formation (Figure 1b). This fact confirms the exciplex nature of the appearance of the photocurrent.

The study of the spectral dependence of photosensitivity showed that the maximum photocurrent is observed under illumination by light in the region of 350-450 nm, which corresponds to the spectral region of absorption of the materials forming the diode structure. It is of interest to find out which components of the device are responsible for the primary absorption of a light quantum in the formation of the exciplex. For this purpose, we measured the photoluminescence (PL) excitation spectra of thin films containing Zn(TSA-BTZ)$_2$, PTA and their mixture 1:1 by weight, and their PL and absorption spectra (figure 2).

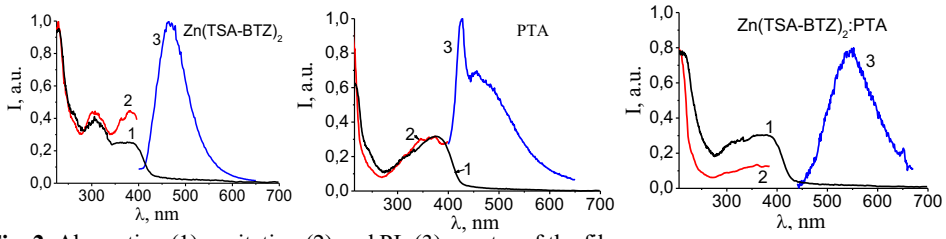

Fig. 2. Absorption (1) excitation (2) and PL (3) spectra of the films.

In the PL spectra of Zn(TSA-BTZ)$_2$ and PTA, bands of the intrinsic PL of these substances are observed respectively at 470 nm and 425-460 nm, while the exciplex band at 550 nm is observed in the PL spectrum of the mixture. In the absorption and the excitation spectra of the film of pure Zn(TSA-BTZ)$_2$ complex, a band around 300 nm is observed. Such band is absent in the absorption and the excitation spectra of PTA. Herewith the absorption band around 300 nm is present in the absorption spectrum of the mixture, which is obviously due to the absorption of Zn(TSA-BTZ)$_2$ molecules. However, this band is absent in the excitation spectrum of the mixture. This is due to the exciplex nature of the fluorescence of the mixture. One may suppose that in the case of PL of the mixture, the primary excitation occurs on the PTA molecule with subsequent electron transfer to an excited level of the Zn(TSA-BTZ)$_2$ molecule and then the radiative recombination with the hole on the main level of PTA. In the case of photocurrent in the device based on Zn(TSA-BTZ)$_2$ and PTA, the primary excitation obviously occurs also on the molecule of the hole transport layer PTA with subsequent separation and transport of charge carriers to the electrodes.

Thus we show that the diode structures described in ref. [1,2] as OLEDs are also characterisrd by photosensitivity properties. which is associated with the formation of exciplexes. The primary process in the photosensitivity is the photoexcitation of the molecules of the hole-transporting layer.

This work was supported by Russian Foundation for Basic Research (16-33-01091).

References

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