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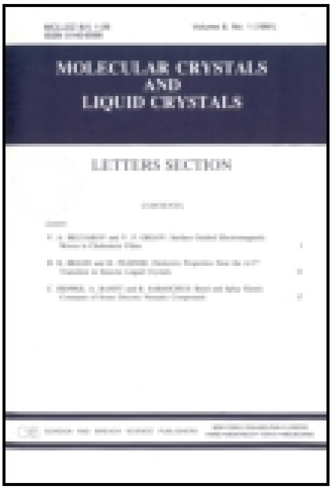

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The Electroluminescence Spectra of Light-Emitting Devices Based on Zinc Complexes of Amino-Substituted Ligands

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The Electroluminescence Spectra of Light-Emitting Devices Based on Zinc Complexes of Amino-Substituted Ligands

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Exciplex bands in the electroluminescence (EL) spectra of electroluminescent devices based on the new zinc complexes of amino-substituted benzothiazoles and in the photoluminescence (PL) spectra of the blends of a zinc complex and the triphenylamine derivative are studied. For the EL spectra, it is found that the relation between the exciplex bands and the intrinsic bands of the zinc complex emission depends on the thickness of layers in the EL devices and on the applied voltage. For the PL spectra of blends, this relation strongly depends on the concentration of components.

Keywords Amino-substituted benzothiazoles; electroluminescence; exciplex; photoluminescence; zinc complexes; triphenylamine

Introduction

Recently, the emission spectra of electroluminescent devices based on the new zinc complexes of amino-substituted benzothiazoles and quinolines containing the C-N-M-N chains in their chelate cycles were investigated [1–3]. The electroluminescence (EL) spectra exhibit strong exciplex bands in the green to yellow region 540 to 590 nm due to the interaction of the excited states of zinc complexes and triaryl molecules of a hole-transporting layer. For some devices, the intrinsic luminescence band of 460 nm in the blue region is also observed along with the exciplex band giving rise to an almost white color of the device emission. Exciplex emission can also be observed in the photoluminescence (PL) spectra of the films containing blends of the zinc complex and a hole-transporting material [2, 3]. The combination of a narrow intrinsic band and a wide exciplex band gives a very wide spread of emission over the whole visible spectrum, which is a way to obtain white light emission [1–3].

The main reason for the effective formation of exciplexes for these compounds is probably the presence of a spatially extended, electron-rich amine segment in the zinc complex molecule, which can enhance its ability of intermolecular interactions with molecules of the hole-transporting layer and hence can magnify the possibility of the exciplex formation. A material of the hole-transporting layer is crucial for the exciplex formation efficiency. Triarylamine derivatives seem to be the most proper materials for the exciplex formation [1–3].

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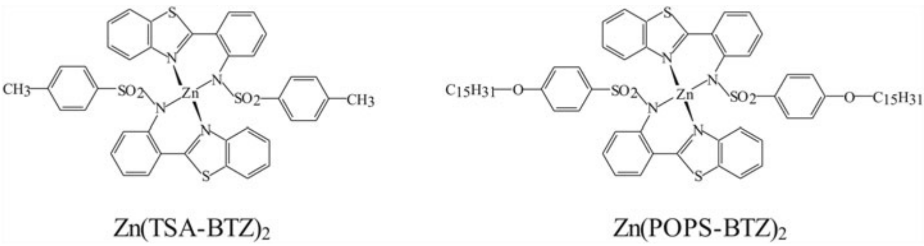


Scheme 1. Molecular structures of studied zinc complexes.

In the present work, we will perform a more comprehensive study of the exciplex spectra for two zinc complexes of amino-substituted benzothiazoles Zn(TSA-BTZ)$_2$ and Zn(POPS-BTZ)$_2$:

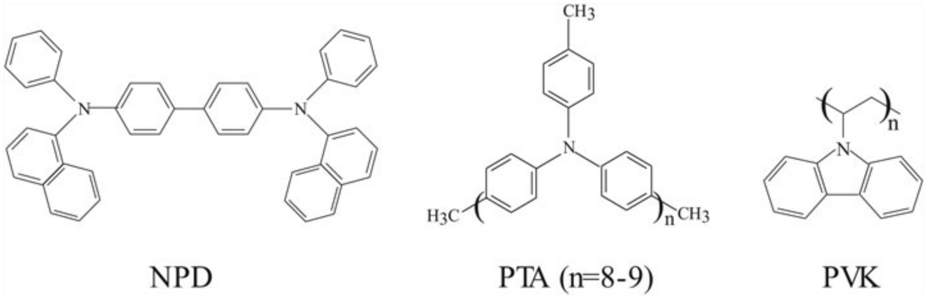
We studied the dependence of the intrinsic and exciplex EL bands of the EL devices on the thickness of hole-transporting layers and on the applied voltage. We also studied the dependence of the exciplex bands in the PL spectra of blends of the zinc complex and a material of hole-transporting layer on the ratio of components.

Experimental

Electroluminescence was observed for the layered structures containing the transparent anode of indium-tin oxide (ITO), organic hole-transporting layer, the luminescence layer of one of the studied complexes, and the metallic cathode of Al:Ca alloy. The hole-transporting materials used were triarylamine derivatives - well-known naphthyl-substituted benzidine derivative (NPD) and the oligomer of triphenylamine oligo(4,4'-(4"-methyl)triphenylamine) (PTA) [4]. Layers of PTA were prepared by the spin-coating from a toluene solution. Other layers were prepared by the vacuum sublimation.

The photoluminescence spectra were observed for the films containing blends of the zinc complex and PTA or the zinc complex, PTA, and poly(9-vinylcarbazole) (PVK) in different proportions. Films were prepared from toluene, chloroform, or chlorobenzene solutions containing the components in proper concentrations.

The EL and PL spectra were measured with an Ocean Optics fiber optics spectrometer QE65000. LED with $\lambda = 380$ nm was used to excite PL.



Scheme 2. Molecular structures of studied hole-transporting materials.

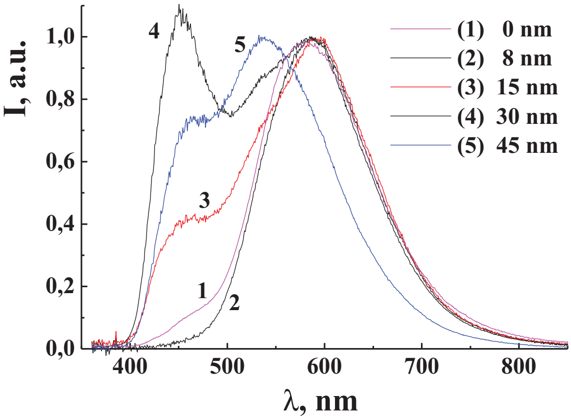


Figure 1. Normalized EL spectra of ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca devices with different thicknesses of the NPD layer: 0 (1), 8 (2), 15 (3), 30 (4), and 45 nm (5). Spectra are measured at the same current 7.4 mA/cm^2 for all devices.

Results and Discussion

The relation between intrinsic and exciplex bands in the EL spectra of electroluminescent devices containing the NPD/Zn(TSA-BTZ)$_2$ interface

Some of the EL devices based on amino-substituted zinc complexes (in particular, the devices with PTA as a hole-transporting layer contacting with the zinc complex) demonstrate the EL spectra containing only the exciplex bands, while other devices demonstrate the intrinsic EL bands [1–3]. The relation between intrinsic and exciplex bands can be affected by different factors: materials of contacting layers [5], thicknesses of layers [6–10], applied voltage, and current [11–13]. We have studied the dependence of the relation between intrinsic and exciplex bands in the EL spectra of the devices based on amino-substituted zinc complexes on the thickness of a hole-transporting layer and on the applied bias voltage for the devices based on Zn(TSA-BTZ)$_2$ as an illustrative example.

Figures 1 and 2 show the EL spectra of the devices ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca with different thicknesses of the NPD layer: 0, 8, 15, 30, and 45 nm. Thicknesses of other organic layers are constant: about 100 nm for PTA and about 30 nm for Zn(TSA-BTZ)$_2$. Spectra are measured at different bias voltages from 3.5 V to 10 V.

The shape of the EL band strongly depends on the NPD layer thickness (Fig. 1). For thicknesses of 8, 15, and 30 nm, the exciplex band with maximum near 590 nm is observed. The further increase in the thickness leads to some shift of the exciplex band maximum position. For the thickness of 45 nm, the exciplex band in the region of 540 nm is observed. The device with an NPD layer 8 nm in thickness exhibits no intrinsic band in the EL spectra, as well as the device with no NPD layer. Devices with NPD layer thicknesses of 15, 30, and 45 nm exhibit the intrinsic EL band in the region of 450-460 nm in addition to exciplex bands. Note that all the components of the device, PTA, NPD, and Zn(TSA-BTZ)$_2$, are characterized by the intrinsic luminescence in the region of 430–460 nm [1–4].

Figure 2 shows the dependence of the EL spectra of Zn(TSA-BTZ)$_2$ based devices with different thicknesses of a hole-transporting NPD layer on the applied bias voltages and the corresponding currents through the device. As the voltage increases, the maximum of theexciplex band shifts to lower wavelengths by 5-8 nm, whereas the maximum of

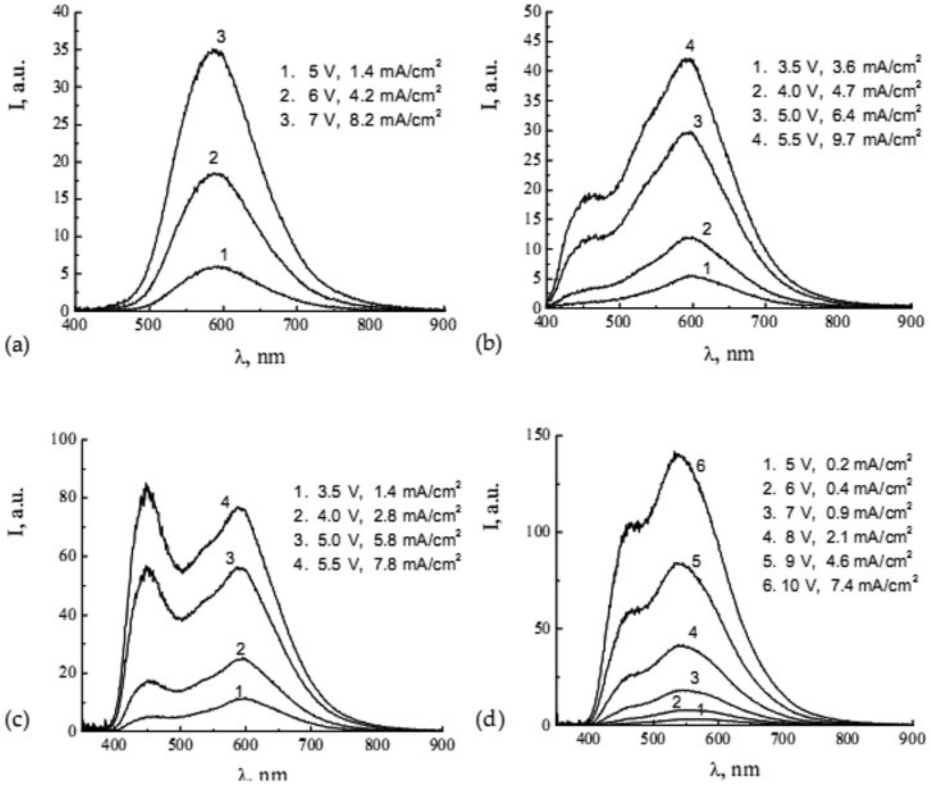


Figure 2. EL spectra of the devices ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca with different thicknesses of the NPD layer: 8 (a), 15 (b), 30 (c), and 45 nm (d). The applied bias voltages and the currents through the device are given along with curve numbers.

the intrinsic band practically does not change. The increasing voltage leads also to the appearance of an additional exciplex peak at 540 nm in the EL spectra of the devices with the NPD layer 15 and 30 nm in thickness (Fig. 2b, c).

The shift of exciplex bands maxima with changes in the layer thickness and the applied voltage may be due to the plurality of excited states in the excited donor-acceptor complexes [14, 15]. In our case, these states may be due to the interaction of both PTA and NPD with Zn(TSA-BTZ)$_2$. It is known that the exciplex bands are observed in the electroluminescence spectra of the devices based on zinc complexes of amino-substituted ligands with hole-transporting layers consisting of both PTA (without NPD) and NPD (without PTA) [1–3].

The ratio of the intensities of intrinsic and exciplex bands depends on the applied bias voltage and the corresponding currents. With increasing the voltage, the intensity of the intrinsic band relative to that of the exciplex band increases. For the device with a NPD layer 30 nm in thickness, the intrinsic band becomes more intense than the exciplex band at some voltages. The growth of the intrinsic band can be attributed to a shift of the carrier recombination zone from the NPD/Zn(TSA-BTZ)$_2$ interface to the bulk of the emitter layer and to the increasing number of holes injected into the emitter layer due to the increasing electric field [7, 12, 16].

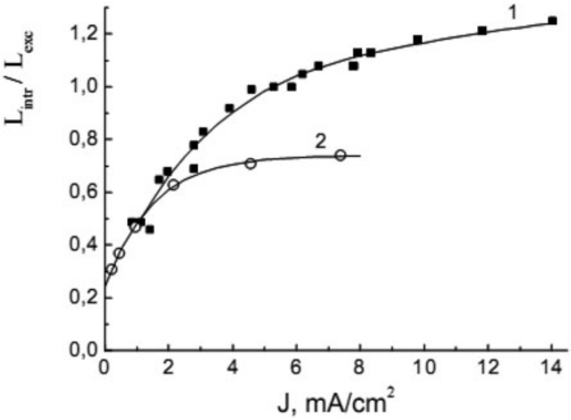


Figure 3. Plot of relative intensities of the intrinsic EL band and that of the exciplex band as a function of the current for the devices ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca with the NPD layer with thicknesses of 30 nm (1, squares) and 45 nm (2, circles). Solid curves represent only guide to an eye.

It should be noted that the electroluminescence intensity depends on the number of recombinating electrons and holes, i.e., on the current through the device. So the dependence of the EL spectra on the applied bias voltage should more properly be considered as the dependence on the current. Figure 3 shows the ratio of the intensities of the intrinsic EL band (L_{intr}) and that of the exciplex band (L_{exc}) for the devices with the NPD layers 30 and 45 nm in thickness, depending on the current. The intensity of the intrinsic band relative to that of the exciplex band increases with the current and saturates at large currents. The saturation may be due to extending the carrier recombination zone to the whole Zn(TSA-BTZ)$_2$ layer. This saturation takes place for the 30-nm thickness at the ratio L_{intr} / L_{exc} greater than 1 and for the 45-nm thickness at the ratio L_{intr} / L_{exc} less than 1. This difference may be probably due to different nature of exciplex states.

PL spectra of the blends containing PTA and Zn(TSA-BTZ)$_2$ or Zn(POPS-BTZ)$_2$

It is known that exciplexes can also be observed in the PL spectra of donor-acceptor blends [17–21]. On the other hand, another sort of bimolecular excited complexes called the electroplex can be generated around a heterojunction in the EL device. Unlike the exciplex emission that can be observed under both photo-excitation and electric-field excitation, the electroplex emission cannot be typically observed under photo-excitation and can be formed only in the presence of a high electric field in some OLEDs [22–25]. Thus, the study of the PL spectra of the blends of the zinc complexes and tiarylamines may prove the exciplex nature of long-wavelength bands in the emission spectra.

In this paper, we studied the PL spectra of the films containing blends of PTA and Zn(TSA-BTZ)$_2$ or PTA and Zn(POPS-BTZ)$_2$. In some cases, both the zinc complex and PTA were mixed with PVK polymer. The mass ratios between PTA and the Zn complex were equal to 100:0 (only PTA); 82:18; 50:50; 18:82; 0:100 (only Zn complex).

Figure 4 shows the normalized PL spectra of films containing Zn(TSA-BTZ)$_2$ and PTA. Figure 5 shows the normalized PL spectra of the films containing Zn(POPS-BTZ)$_2$ and PTA. Only-PTA films are characterized by strong PL of PTA with maximum at about 440-460 nm.

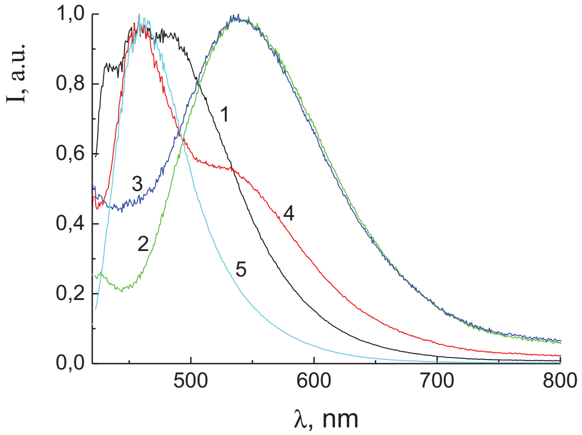


Figure 4. Normalized PL spectra of the films containing Zn(TSA-BTZ)$_2$ and PTA. The ratios of PTA and the Zn complex: 1 – only PTA; 2 – 82:18; 3 – 50:50; 4 – 18:82; 5 – only the Zn complex.

For the films with Zn(TSA-BTZ)$_2$ (Fig. 4), a small admixture of this complex to PTA (18% of the complex) leads to an abrupt drop of the PTA PL intensity and to the appearance of a strong exciplex maximum at about 540 nm with no intrinsic PL band of Zn(TSA-BTZ)$_2$. For the system without PVK, the maximal intensity of the exciplex band is achieved at 18%-50% of the zinc complex. The further increase in the concentration of the complex leads to a decrease in the exciplex band intensity and the growth of the intrinsic PL band of Zn(TSA-BTZ)$_2$ at about 460 nm.

For the films with Zn(POPS-BTZ)$_2$ (Fig. 5), the exciplex band is much less pronounced and manifests itself as a shoulder in the region of 540-550 nm. The maximum intensity of the exciplex band is achieved at 18 and 50% of the zinc complex for the films without PVK and with PVK, correspondingly. The intrinsic PL band of Zn(POPS-BTZ)$_2$ is more intense than the exciplex band. The lower intensity of the exciplex band for the films

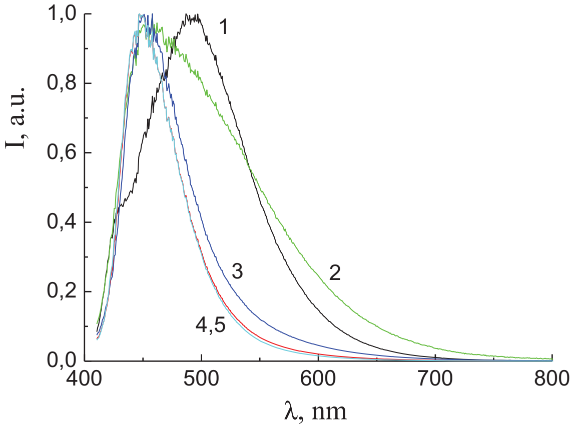


Figure 5. Normalized PL spectra of the films containing Zn(POPS-BTZ)$_2$ and PTA. The ratios of PTA and the Zn complex: 1 – only PTA; 2 – 82:18; 3 – 50:50; 4 – 18:82; 5 – only the Zn complex.

with Zn(POPS-BTZ)$_2$ comparing to that of Zn(TSA-BTZ)$_2$ can be explained by steric restrictions for the contacts between PTA and Zn(POPS-BTZ)$_2$ molecules due to the long aliphatic tail of Zn(POPS-BTZ)$_2$ molecule.

Conclusions

The zinc complexes of amino-substituted benzothiazoles are characterized by strong exciplex bands in their EL and PL spectra. The relation between exciplex and intrinsic bands depends on many factors: material and thickness of layers in the EL devices, concentration of components in mixed films, and so on. Thus, these complexes can be used as components in the EL devices of different emission colors.

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