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Exciplex Electroluminescence Spectra of the New Organic Materials Based on Zinc Complexes of Sulphanylamino-Substituted Ligands

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The emission spectra of the electroluminescent devices based on novel zinc complexes of sulphonylamino substituted quinolines, 2-phenylbenzazoles, and oxadiazoles are reported. The spectra exhibit wide intensive bands probably of exciplex nature. The exciplex formation can probably be due to the interaction of nitrogen atoms of amino substituents of a zinc complex and amino-containing molecules of a hole-transporting layer.

Keywords Amino substitution; exciplex; organic electroluminescence; white light; zinc complexes

Introduction

Light-emitting diodes based on organic electroluminescent materials (OLEDs) are the subject of intensive studies in the recent time due to their potential use in practice in flat displays and as light sources [1–5]. At the same time, these systems are of great interest from the standpoint of the physics of processes running in them, in particular, the mechanisms of light emission.

It is well known that the electroluminescence (EL) spectra of most of the organic materials are similar to their photoluminescence (PL) spectra. This is due to the fact that the same energy levels are involved in the EL and PL processes. An exception from this rule can arise when the exciplex formation in an electroluminescent material is possible [6]. We found that the new electroluminescent materials based on new zinc complexes of sulphanilamino-containing ligands exhibit the EL spectra differing significantly from the PL ones, which can be explained by the exciplex formation [7].

The aim of this work is a more detailed investigation of the exciplex formation in the systems containing metal complexes of such a type. We have measured the EL and PL spectra of the electroluminescent devices and films based on novel

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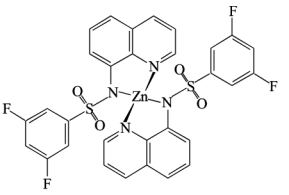
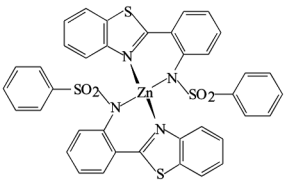
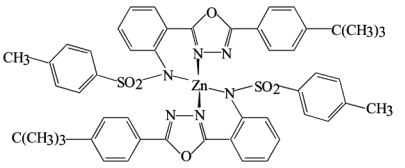
zinc complexes of sulphanilamino-substituted quinolines, benzothiazoles, and oxadiazoles [7–10]:



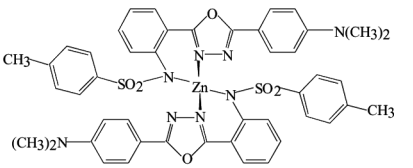
$Zn(DFP\text{-}SAMQ)_2$



$Zn(PSA\text{-}BTZ)_2$



$Zn(TB\text{-}ODZ)_2$



$Zn(DMA\text{-}ODZ)_2$

These complexes are analogs of the well-known zinc complexes with hydroxy substituted ligands ZnQ_2, $Zn(BTZ)_2$, and $Zn(ODZ)_2$ [11–13]. In our complexes, the oxygen atoms in a chelate cycle are replaced by nitrogen atoms of a sulfonylamine fragment. While for the oxygen analogs, the PL and EL spectra are almost identical [11–13], the aminosubstituted complexes exhibit the EL spectra with additional exciplex bands.

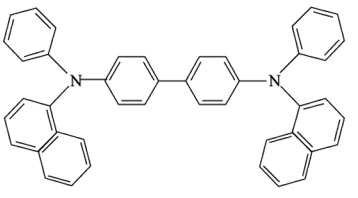
Experimental

Spectral Properties

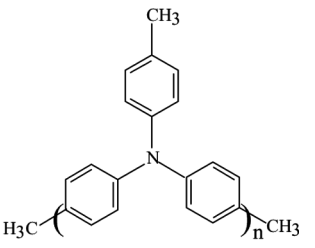
The PL spectra of powders and films of the complexes and the EL spectra of the devices were measured on Ocean Optics PC1000 and Ocean Optics QE65000 spectrometers in the region of 350–800 nm. For the PL excitation, a light-emitting diode with emission at 370 nm was used.

Preparation of Electroluminescence Devices

Glass supports covered with patterned indium—tin oxide (ITO) were used as anodes. Either NPD (NPB) [1,14] or triphenylamine oligomer PTA [15] (or both) were deposited on the anode as hole-transporting layers.

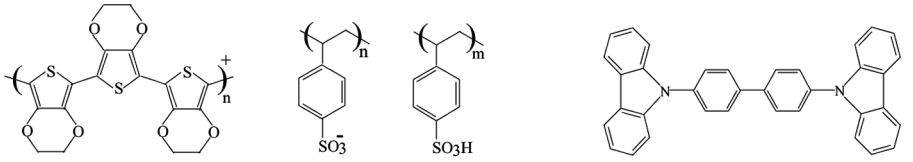


NPD



PTA (n = 8-9)

PTA was deposited by the spin casting from a solution in toluene, and NPD was deposited by the evaporation in vacuo. Some devices included also layers of polyethylenedioxythiophen doped with polystyrene sulphonate (PEDOT:PSS) [16] or 4,4′-bis(N-carbazolyl)-2,2′-biphenyl (CBP) [5] previous to the emitting layer.



PEDOT-PSS CBP

An emitting layer consisting of one of the complexes under study was deposited on the transporting layer by the evaporation in vacuo. The preparation of a device was completed by the vacuum sputtering of a metallic cathode of Al:Ca alloy (~20:1 wt:wt). Parts of the device where the organic layer is not covered with a metal were used for measuring its PL spectra. The procedures in vacuo were carried out at a basic pressure of $5 \cdot 10^{-6}$ Torr. The surface area of the emitting part of the device was ~4 mm^2.

Results and Discussion

Zn(PSA-BTZ)$_2$ Spectra

Figure 1 shows the EL spectra of Zn(PSA-BTZ)$_2$ in two electroluminescence devices ITO/PTA/NPD/Zn(PSA-BTZ)$_2$/Al:Ca (device 1, Fig. 1a, curve 1) and ITO/PTA/Zn(PSA-BTZ)$_2$/Al:Ca (device 2, Fig. 1b, curve 1). For comparison, Figure 1a (curve

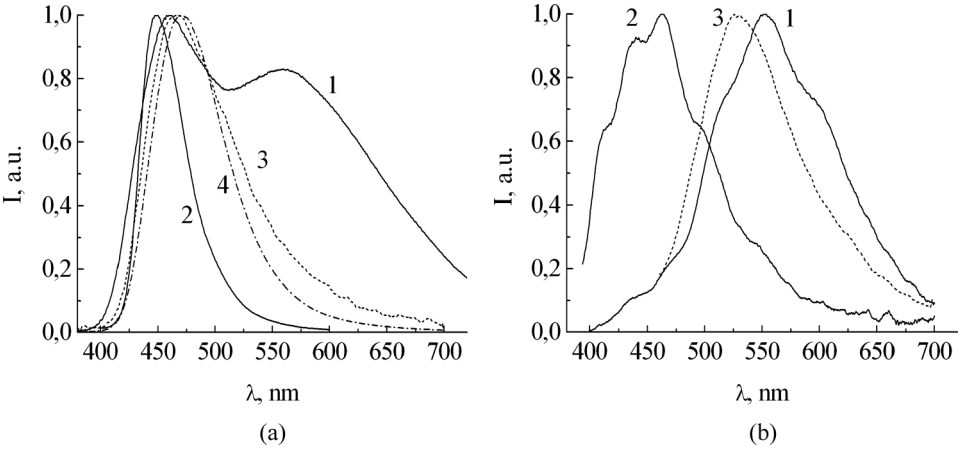


Figure 1. (a) EL spectrum of device 1 ITO/PTA/NPD/Zn(PSA-BTZ)$_2$/Al:Ca (1); PL spectrum of Zn(PSA-BTZ)$_2$ powder (2); EL spectrum of ITO/PTA/NPD/CBP/Zn(PSA-BTZ)$_2$/Al:Ca (3), and EL spectrum of ITO/PEDOT:PSS/Zn(PSA-BTZ)$_2$/Al:Ca (4), (b) EL (1) and PL (2) spectra of device 2 ITO/PTA/ Zn(PSA-BTZ)$_2$/AlCa sample; PL of a mixed PTA:Zn(PSA-BTZ)$_2$ film.

2) shows the PL spectrum of $Zn(PSA\text{-}BTZ)_2$ powder, and Figure 1b (curve 2) does the PL spectrum of the device, i.e., the three-layer structure ITO/PTA/$Zn(PSA\text{-}BTZ)_2$, which combines the PL spectra of PTA and $Zn(PSA\text{-}BTZ)_2$. The EL spectrum of device 1 contains two bands with maxima at 460 and 560 nm. The maximum of the first band is close to that of the PL peak of $Zn(PSA\text{-}BTZ)_2$ powder at 450 nm and can be attributed to the intrinsic luminescence of $Zn(PSA\text{-}BTZ)_2$. The second peak can be probably due to the exciplex formation between NPD and $Zn(PSA\text{-}BTZ)_2$. The EL spectrum of an analogous device ITO/NPD/$Zn(PSA\text{-}BTZ)_2$/Al:Ca (without PTA) was reported previously [7] and also contained both the intrinsic and exciplex bands. For device 2, the EL spectrum exhibits only the wide band with a maximum at 553 nm which can be attributed to the exciplex formation between PTA and $Zn(PSA\text{-}BTZ)_2$.

An exciplex can be formed between the ground state of a donor molecule and an excited state of an acceptor molecule [6]. In our case, a donor molecule is presented by NPD or PTA and an acceptor molecule by $Zn(PSA\text{-}BTZ)_2$ complex. The exciplex band corresponds to the transition from the excited state of the acceptor and the ground state of the donor and has a lower transition energy compared to the intrinsic emission band corresponding to the transition between the excited and ground states of the acceptor molecule [6]. The combination of a narrow intrinsic band and a wide exciplex band gives a very wide emission spread over the whole visible spectrum which is a way to obtain white light emitting diodes [6,7,18].

It should be noted that both NPD and PTA, as well as many other materials usually used to form a hole-transporting layer, are the derivatives of triarylamines. One may suppose that the interaction of the amine-like nitrogen atoms of hole-transporting molecules and the amino groups of zinc complexes determines the exciplex formation in the studied systems. The evidence in favor of this supposition comes from our results on using other materials for hole-transporting layers different from triparylamine derivatives. Figure 1a (curve 4) shows the EL spectrum of a device ITO/PEDOT:PSS/$Zn(PSA\text{-}BTZ)_2$/Al:Ca, where the hole-transporting layer is presented by PEDOT:PSS which is a material injecting and transporting holes, and it does not contain nitrogen atoms at all [16]. This spectrum contains no wide band around 560 nm and exhibits only one band with a maximum at 466 nm which is close to the $Zn(PSA\text{-}BTZ)_2$ powder PL band (450 nm) and can be attributed mainly to the intrinsic emission of the $Zn(PSA\text{-}BTZ)_2$ complex. One may suppose that the formation of an exciplex in this case is suppressed by the absence of nitrogen atoms in the hole-transporting layers.

Another way to suppress the exciplex formation is to put an additional layer between NPD and the zinc complex. Figure 1a (curve 3) shows the EL spectrum of a device ITO/NPD/CBP/$Zn(PSA\text{-}BTZ)_2$/Al:Ca. This spectrum also contains no wide band around 560 nm and exhibits only one band with a maximum at 471 nm which can be attributed mainly to the intrinsic emission of the $Zn(PSA\text{-}BTZ)_2$ complex. CBP is a carbazole derivative which is used as a conducting layer in OLEDs [5]. The suppression of the exciplex formation in this case can be related to the non-amine nature of a nitrogen atom in the carbazole fragment of CBP. A similar result was obtaind in [18], where the nitrogen-containing analog of Alq_3 exhibits exciplex EL bands in the devices with NPD as a hole-transporting layer. The intermediate layer of another carbazole derivative (1,3-bis(9-carbazolyl)-benzene, mCP) suppresses the exciplex emission [18].

If the exciplex between a zinc complex and a donor molecule such as PTA is formed, it must be observed not only in the EL spectra, but in the PL spectra too. However, as seen from Figure 1b, the PL emission of device 2 (curve 2) exhibits no exciplex band observed in the EL spectrum (curve 1). Only the PL band with a maximum at 463 nm corresponding to the intrinsic PL of the materials of both organic layers is observed. The EL emission arises at the interface of the hole-transporting layer and the luminescence layer, while the PL emission is excited in the bulk of the sample. A possible exciplex PL band is not observed because of the extreme thinness of the interface layer, where exciplex can be formed.

To observe the PL from an exciplex, we have prepared a mixed film containing PTA and Zn(PSA-BTZ)$_2$ complex in the approximately 1:1 wt:wt ratio in the bulk of the film. The film was prepared by the casting from a toluene solution containing both components in appropriate concentrations. Figure 1b, curve 3 shows the PL spectrum of the mixed film. The wide band with a maximum at 525 nm is observed like the EL exciplex band of device 2 containing the PTA/Zn(PSA-BTZ)$_2$ interface (curve 1). No bands in the region of 450 nm characteristic of the intrinsic emission of the components is observed in the PL of the mixed film, as well as in the EL of device 2. All this is the evidence of the strong exciplex interaction in the PTA/Zn(PSA-BTZ)$_2$ system.

Zn(DFP-SAMQ)$_2$ Spectra

Figure 2 shows the EL spectra of Zn(DFP-SAMQ)$_2$ in two electroluminescence devices ITO/PTA/NPD/Zn(DFP-SAMQ)$_2$/Al:Ca (device 3, Fig. 2a, curve 1) and ITO/PTA/Zn(DFP-SAMQ)$_2$/Al:Ca (device 4, Fig. 2b, curve 1). For comparison, Figure 2a (curve 2) shows the PL spectrum of Zn(DFP-SAMQ)$_2$ powder (maximum at 465 nm), and Figure 2b (curve 2) presents the PL spectrum of the three-layer structure ITO/PTA/Zn(DFP-SAMQ)$_2$ of device 4 which combines the PL spectra of PTA and Zn(DFP-SAMQ)$_2$. The EL spectra of devices 3 and 4 contain each one band with maxima at 553 nm and 550 nm, respectively, which can be probably due

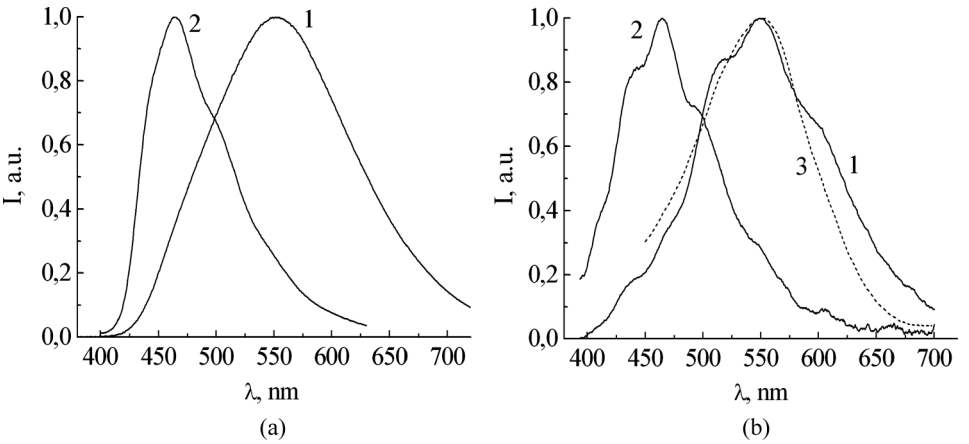


Figure 2. (a) EL (1) and PL (2) spectra of device 3 ITO/PTA/NPD/Zn(DFP-SAMQ)$_2$/Al:Ca; (b) EL (1) and PL (2) spectra of device 4 ITO/PTA/Zn(DFP-SAMQ)$_2$/Al:Ca; PL of a mixed PTA:Zn(DFP-SAMQ)$_2$ film (3).

to the exciplex formation between NPD or PTA and $Zn(DFP\text{-}SAMQ)_2$. For both devices, no band around 465 nm is observed which could be attributed to the intrinsic luminescence of $Zn(DFP\text{-}SAMQ)_2$.

In Figure 2b, the PL emission of device 4 (curve 2) exhibits only the PL band with a maximum at 465 nm corresponding to the intrinsic PL of the materials of both organic layers. No exciplex band is observed in the PL of the device because of the extremely thin interface layer where an exciplex can be formed.

To observe PL from exciplexes, we have prepared a mixed film containing PTA and $Zn(DFP\text{-}SAMQ)_2$ complexes in the wt:wt ratio of approximately 1:1 in the bulk of the film. The film was prepared by the casting from a toluene solution containing both components in appropriate concentrations. Figure 2b (curve 3) shows the PL spectrum of the mixed film. The wide band with a maximum at 550 nm is observed similar to the EL exciplex band of device 2 containing the PTA/$Zn(DFP\text{-}SAMQ)_2$ interface (curve 1). No bands in the region of 465 nm characteristic of the intrinsic emission of the components are observed in the PL of the mixed film, as well as in the EL of device 4. All this is the evidence of the strong exciplex interaction in the PTA/$Zn(DFP\text{-}SAMQ)_2$ system.

Spectra of Materials Based on Oxadiazoles

Figure 3 shows the EL spectra of $Zn(TB\text{-}ODZ)_2$ in two electroluminescence devices ITO/PTA/NPD/$Zn(TB\text{-}ODZ)_2$/Al:Ca (device 5, Fig. 3a, curve 1) and ITO/PTA/$Zn(TB\text{-}ODZ)_2$/Al:Ca (device 6, Fig. 3b, curve 1). For comparison, Figure 3a (curve 3) shows the PL spectrum of $Zn(TB\text{-}ODZ)_2$ powder (maximum at 405 nm). Figures 3a (curve 2) and 3b (curve 2) show the PL spectra of the four-layer structure ITO/PTA/NPD/$Zn(TB\text{-}ODZ)_2$ of device 5 and the three-layer structure ITO/PTA/$Zn(TB\text{-}ODZ)_2$ of device 6, respectively. Each of the EL spectra of devices 4 and 5 contains two bands. The wide bands with maxima at 475 nm and 490 nm, respectively, can probably arise due to the exciplex formation between NPD or PTA and $Zn(TB\text{-}ODZ)_2$. The shoulder at 440 nm (curve 1, Fig. 3a) and the small maximum

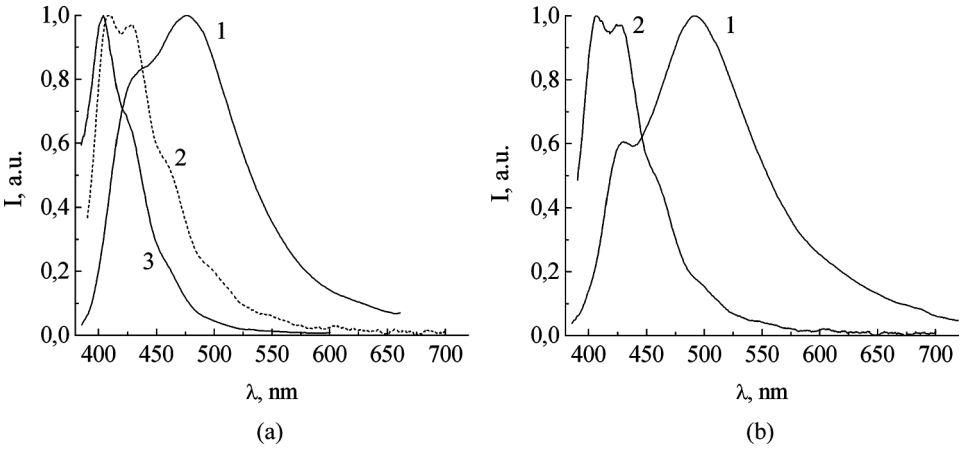


Figure 3. (a) EL (1) and PL (2) spectra of device 5 ITO/PTA/NPD/$Zn(TB\text{-}ODZ)_2$/Al:Ca; PL of $Zn(TB\text{-}ODZ)_2$ powder (3), (b) EL (1) and PL (2) spectra of device 6 ITO/PTA/$Zn(TB\text{-}ODZ)_2$/Al:Ca.

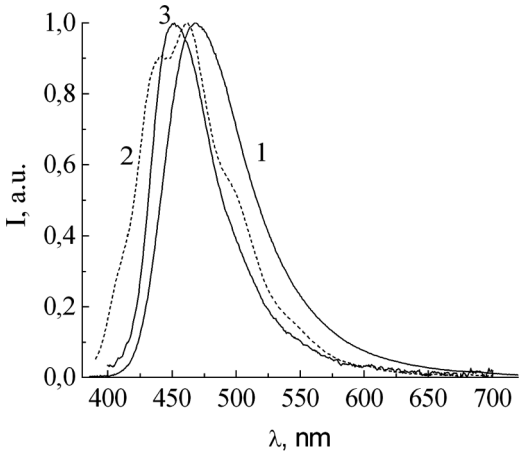


Figure 4. EL (1) and PL (2) spectra of device 7 ITO/PTA/NPD/Zn(DMA-ODZ)$_2$/Al:Ca; PL spectrum of Zn(DMA-ODZ)$_2$ powder (3).

at 430 nm (curve 1, Fig. 3b) are probably due to the intrinsic Zn(TB-ODZ)$_2$ emission. The PL spectra of devices 5 and 6 combine the PL spectra of PTA, NPD, and Zn(TB-ODZ)$_2$ and contain no exciplex bands.

Figure 4 shows the EL spectra of Zn(DMA-ODZ)$_2$ in the electroluminescence device ITO/PTA/NPD/Zn(DMA-ODZ)$_2$/Al:Ca (device 7, curve 1). For comparison, the PL spectra of Zn(DMA-ODZ)$_2$ powder (curve 3) and the four-layer structure ITO/PTA/NPD/Zn(DMA-ODZ)$_2$ of device 7 (curve 2) are shown. The EL spectrum of device 7 contains the single band with a maximum at 470 nm which is close to that of Zn(DMA-ODZ)$_2$ PL (maximum at 452 nm) and can be attributed mainly to the intrinsic emission of the Zn(DMA-ODZ)$_2$ complex. The exciplex emission in the case of device 7 based on Zn(DMA-ODZ)$_2$, if exists, has a very small intensity, and the displacement of its spectrum is small. The nature of this distinction of Zn(DMA-ODZ)$_2$ from other aminosubstituted complexes under study is not clear yet. The PL spectrum of device 7 (curve 2), like the PL of the other studied devices, contains no exciplex band.

Conclusions

In summary, the electroluminescence devices based on the aminosubstituted zinc complexes as an electron conducting emitting layer and triaryl derivatives as a hole-transporting layer exhibit the EL spectra with the exciplex emission in addition to the intrinsic EL bands or even instead of the intrinsic bands. The exciplex formation is probably determined by the interaction of the amine-like nitrogen atoms of hole-transporting molecules and the amino groups of zinc complexes. This can be approved by the following facts: 1) for the oxygen analogs of the studied complexes (with no amine nitrogen atoms), the PL and EL spectra coincide even with triaryl derivatives as hole-transporting layers [11–13]; 2) the EL exciplex bands disappear when no amine-like nitrogen is present in the hole-transporting layer; and 3) the exciplex band appears in the PL spectra of mixed films containing the aminosubstituted zinc complexes and the amine-like hole transporting material.

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