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Exciplex Electroluminescence of the New Organic Materials for Light-Emitting Diodes

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http://dx.doi.org/10.5772/51799

1. Introduction

In typical organic light emitting devices (OLEDs), light originates from radiative recombination of molecular excited states formed by electrons and holes injected from electrodes and localized on individual molecular sites. That is, the results are interpreted as due to Frenkel exciton generation and recombination [1,2]. In particular, this is applied to the bilayer OLEDs composed of metal 8-hydroxyquinolates M$_3$Q$_3$ (M = Al, Ga, In, or Sc) as an electron-transporting and emitting layer and amines like triphenylamine derivative (TPD) as a hole-transporting layer. The electroluminescence (EL) spectra of these devices are close to the photoluminescence (PL) spectra of corresponding M$_3$Q$_3$ molecules [1-3]. The similarity of the EL and PL spectra was also observed for zinc complexes with hydroxy-substituted quinolines, benzothiazoles and related ligands [4-6].

In some bilayer devices, interactions of donor and acceptor molecules at the organic/organic interface can lead to formation of an exciplex state. Exciplex is a kind of excited state complex formed between donor and acceptor, with one in the excited state and the other in the ground state. Exciplex usually leads to the red shifted emission and broadened spectrum relative to the emissions of the individual acceptor or donor [7-10].

Exciplex formation at the solid interface between Alq$_3$ and the electron-rich multiple triarylamine hole-transporting materials m-MTDATA and t-Bu-TBATA was observed in a study by Itano et al., [11]. Exciplexes can also be observed in the PL spectra of donor-acceptor blends [10,12-15].

Sometimes, another sort of bimolecular excited complex called electroplex can be generated around heterojunction. Unlike exciplex emission which can be observed under both photo-excitation and electric field excitation, electroplex emission can not be typically observed under photo-excitation and can be formed only in the presence of high electric field in some OLEDs. [16-19].
The intrinsic luminescence of the emitting layer is quenched by the formation of exciplexes [20-24]. So, for pure monochromatic OLEDs, exciplexes should be avoided [25-27]. On the other hand, exciplexes were proposed to tune the OLED emission color [28-30] and to design white OLEDs [12,18,31-35]. The use of exciplex emission simplifies the structure of white OLEDs. Efficient white electroluminescence from a double-layer device based on a boron complex was demonstrated by Liu et al. [36]. High-efficiency nondoped white organic light-emitting device based on the triarylamine derivative was demonstrated by Tong et al. [37] and Lai et al. [38]. For some OLEDs, pure exciplex emission was obtained by Wang et al. [39] and Nayak et al. [40].

One of the problems in utilizing the exciplex effects in devices is finding systems with high exciplex EL efficiency, so design of new materials and investigation of the active factors for efficient exciplex emission are a subject of significance.

Recently, spectral properties of the electroluminescent devices based on the novel zinc-chelate complexes of sulphanilamino-substituted quinolines and benzothiazoles were investigated and some exciplex phenomena were found [41-46]. The structures of zinc complexes are shown in Figure 1.

Most presently known metal complexes used for OLEDs contain the chelate cycles including the C-O-M-N chains [2-4,6,22,27,47]. In the amino-substituted complexes, the oxygen atom in the chelate cycles is replaced by a nitrogen atom of the sulphanilamino groups forming the C-N-M-N chains. The presence of a spatially extended, electron-rich amine segment in the zinc complex molecule can enhance its ability of intermolecular interactions with the molecules of the hole-transporting layer and hence magnify the possibility of exciplex forming. This chapter presents a review of electroluminescent properties of sulphanilamino-substituted zinc complexes.

2. EL spectra of OLEDs based on sulphanilamino-substituted zinc-chelate complexes

We have prepared and measured the EL spectra of the following OLED devices based on zinc complexes with sulphanilamino-substituted ligands.

- device D1: ITO/PTA/NPD/Zn(PSA-BTZ)\(_2\)/Al:Ca
- device D2: ITO/PTA/Zn(PSA-BTZ)\(_2\)/Al:Ca
- device D3: ITO/PTA/NPD/CBP/Zn(PSA-BTZ)\(_2\)/Al:Ca
- device D4: ITO/PTA/CBP/Zn(PSA-BTZ)\(_2\)/Al:Ca
- device D5: ITO/PEDOT:PSS/Zn(PSA-BTZ)\(_2\)/Al:Ca
- device D6: ITO/PTA/NPD/Zn(TSA-BTZ)\(_2\)/Al:Ca
- device D7: ITO/PTA/Zn(TSA-BTZ)\(_2\)/Al:Ca
- device D8: ITO/PTA/NPD/Zn(POPS-BTZ)\(_2\)/Al:Ca
- device D9: ITO/PTA/NPD/CBP/Zn(POPS-BTZ)\(_2\)/Al:Ca
- device D10: ITO/PTA/NPD/Zn(DFP-SAMQ)\(_2\)/Al:Ca
- device D11: ITO/PTA/Zn(DFP-SAMQ)\(_2\)/Al:Ca
- device D12: ITO/PTA/CBP/Zn(TSA-BTZ)\(_2\)/Al:Ca
Methods of preparing the devices and measuring their properties are described elsewhere [42-44]. Materials of hole-transporting layer were triaryl derivatives: PTA, oligomer of triphenylamine with high glass-transition temperature [48] and a well-known N,N’-bis(1-naphthyl)-(1,1’-biphenyl) -4,4’-diamine (NPD). The carbazol derivative 4,4’-bis(1-carbazolyl)-1,1’-biphenyl (CBP) and poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) were also used for forming the hole-transporting layer. The structures of these compounds are also shown in Figure 1. In some devices, both PTA and NPD deposited in succession were used as materials for hole-transporting layers. In any case, the EL spectrum of
the device is determined by the hole-transporting material, which is in contact with the zinc complex. The devices are typically characterized by bias voltages of light appearance about 2.5 to 3 V and brightness of $10^3$ cd/m$^2$ at 10 V.

2.1. EL spectra of OLEDs based on Zn(PSA-BTZ)$_2$

Figure 2 shows the EL spectra of Zn(PSA-BTZ)$_2$ in two electroluminescence devices: device D1, ITO/PTA/NPD/Zn(PSA-BTZ)$_2$/Al:Ca, (Figure 2a, curve 1) and device D2, ITO/PTA/Zn(PSA-BTZ)$_2$/AlCa, (Figure 2b, curve 1). For comparison, curve 2 in Figure 2a shows the PL spectrum of Zn(PSA-BTZ)$_2$: powder.

Figure 2. Spectra of Zn(PSA-BTZ)$_2$ in the devices D1 to D5. (a): EL spectrum of the device D1 ITO/PTA/NPD/Zn(PSA-BTZ)$_2$/Al:Ca (1); PL spectrum of Zn(PSA-BTZ)$_2$: powder (2); EL spectrum of the device D3 ITO/PTA/NPD/CBP/Zn(PSA-BTZ)$_2$/Al:Ca (3); EL spectrum of the device D5 ITO/PEDOT:PSS/Zn(PSA-BTZ)$_2$/AlCa (4) (b): EL spectrum of the device D2 ITO/PTA/Zn(PSA-BTZ)$_2$/AlCa (1); EL spectrum of the device D4 ITO/PTA/CBP/Zn(PSA-BTZ)$_2$/AlCa (2)
The EL spectrum of device D1 contains two bands with maxima at 460 and 560 nm. Maximum of the first band is close to that of the PL peak of Zn(PSA-BTZ)$_2$ powder at 450 nm and may be attributed to the intrinsic luminescence of Zn(PSA-BTZ)$_2$. The second peak may be probably due to exciplex formation between NPD and Zn(PSA-BTZ)$_2$. For device D2, the EL spectrum exhibits only wide band with a maximum at 553 nm, which may be attributed to exciplex formation between PTA and Zn(PSA-BTZ)$_2$. Exciplex can be formed between the ground state of a donor molecule and the excited state of an acceptor molecule [12]. In our case, the donor molecule is presented by NPD or PTA, and the acceptor molecule by Zn(PSA-BTZ)$_2$ complex. Exciplex band corresponds to the transition from the excited state of the acceptor and the ground state of the donor and has lower transition energy compared to the intrinsic emission band corresponding to the transition between the excited and ground state of the acceptor molecule [7-10,12].

2.2. EL spectra of OLEDs based on Zn(TSA-BTZ)$_2$

Figure 3 shows the EL spectra of Zn(TSA-BTZ)$_2$ in the electroluminescence devices: (a) device D6, ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca, (b) device D7, ITO/PTA/Zn(TSA-BTZ)$_2$/Al:Ca and device D12, ITO/PTA/CBP/Zn(TSA-BTZ)$_2$/Al:Ca. The PL spectrum of Zn(TSA-BTZ)$_2$ powder is shown for comparison (Figure 3a, curve 2).

For the devices D6 and D7, intensive exciplex EL bands are observed in the yellow region with the maxima around 585 nm. Only a weak shoulder in the region of the intrinsic Zn(TSA-BTZ)$_2$: emission at about 460 nm is observed. For device D7, the EL spectra are shown for different bias voltages from 3.5 to 6.0 V. The spectra are normalized to obtain equal intensities of exciplex bands for all voltages. A small continuous growth of intrinsic emission relative intensity is observed. A small blue shift of exciplex band maximum from 585 nm at 3.5 V to 575 nm at 6.0 V is also observed. This is in contrast with previously reported strong dependence of EL bands positions on bias voltages [11,49,50] where field induced shift of EL band of about 50 nm could be attributed to the overlap of the emission from different excited states. As showed Kalinowski et al. [51], the field dependence of EL spectrum in such systems is a result of electric field mediated interplay among localized (monomolecular) excitons, exciplexes, and electroplexes in conjunction with their specific environment. For the device D12, no exciplex band is observed which is discussed in section 4.

2.3. EL spectra of OLEDs based on Zn(POPS-BTZ)$_2$

Figure 4 shows the EL spectra of Zn(POPS-BTZ)$_2$: in the devices D8 ITO/PTA/NPD/Zn(POPS-BTZ)$_2$/Al:Ca (curves 1) and D9 ITO/PTA/NPD/CBP/Zn(POPS-BTZ)$_2$/Al:Ca (curve 3). The PL spectrum of Zn(POPS-BTZ)$_2$: powder (curve 2) is shown for comparison. Strong exciplex band in the green region with the maximum at about 540 nm and shoulder at about 460 nm due to intrinsic emission of Zn(POPS-BTZ)$_2$: is observed in the
EL spectra of the device D8. The normalized EL spectra are shown for different bias voltages from 4.0 to 6.0 V. A small continuous growth of intrinsic emission relative intensity and a small blue shift of exciplex band maximum from 545 nm at 4.0 V to 535 nm at 6.0 V are also observed. For the device D9, no exciplex band is observed which is discussed in section 4.

Figure 3. Normalized EL spectra of the devices based on Zn(TSA-BTZ)$_2$ and the PL spectrum of Zn(TSA-BTZ)$_2$ powder. (a): Normalized EL spectrum of the device D6 ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca (1) and the PL spectrum of Zn(TSA-BTZ)$_2$ powder (2); (b): Normalized EL spectra of the device D7 ITO/PTA/Zn(TSA-BTZ)$_2$/Al:Ca for bias voltages 3.5 V (blue curve), 4.0, 4.5, 5.0, 5.5 V (black curves) and 6.0 V (red curve) (1) and normalized EL spectrum of the device D12 ITO/PTA/CBP/Zn(TSA-BTZ)$_2$/Al:Ca (2).
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Figure 4. Spectra of Zn(POPS-BTZ)$_2$ based devices: Normalized EL spectra of the device D8 ITO/PTA/NPD/Zn(POPS-BTZ)$_2$/Al:Ca for bias voltages 4.0 V (blue curve), 4.5, 5.0, 5.5 V (black curves) and 6.0 V (red curve) (1), PL of Zn(POPS-BTZ)$_2$ powder (2) and the EL spectrum of the device D9 ITO/PTA/NPD/CBP/Zn(POPS-BTZ)$_2$/Al:Ca (3)

2.4. EL spectra of OLEDs based on Zn(DFP-SAMQ)$_2$

Figure 5 shows the EL spectra of Zn(DFP-SAMQ)$_2$ in the devices D10 ITO/PTA/NPD/Zn(DFP-SAMQ)$_2$/AlCa (curve 1) and D11 ITO/PTA/Zn(DFP-SAMQ)$_2$/AlCa (curve 2). For comparison, the PL spectrum of Zn(DFP-SAMQ)$_2$ powder with maximum at 465 nm is shown (curve 3). Exciplex bands with maxima at about 560 nm and no intrinsic emission are observed in the EL spectra both for devices with both PTA and PTA/NPD hole-transporting layers. Exciplex emission can also be observed in the PL spectra of the films containing blends of zinc complex and hole-transporting material (curve 4) which is discussed in section 3.

Figure 5. Spectra of Zn(DFP-SAMQ)$_2$ based devices: EL spectra of the devices D10 ITO/PTA/NPD/Zn(DFP-SAMQ)$_2$/AlCa (1) and D11 ITO/PTA/Zn(DFP-SAMQ)$_2$/AlCa (2); PL spectra of Zn(DFP-SAMQ)$_2$ powder (3) and of PTA:Zn(DFP-SAMQ)$_2$ mixed film (4).
3. The PL spectra of the films containing blends of zinc complex and of hole-transporting material

One of the main evidences of the exciplex nature of long-wave bands in the EL spectra is the presence of such bands in the PL spectra of blends of donor and acceptor materials [12-15,17,40,53].

For the zinc-chelate complexes with sulphanilamino-substituted ligands, the exciplex long-wave bands were observed in the PL spectra of their blends with hole-transporting materials by Kaplunov et al. [44-45]. It was shown previously that the PL spectra taken from the layered structure exhibiting the exciplex EL OLEDs do not contain long-wave bands but only the intrinsic bands of components [46]. This is due to the extremely small thickness of the contacting interface of the two layers, which is responsible for EL. To observe the long-wave bands in PL, films containing blends of zinc complex and hole-transporting material were prepared by casting from toluene solutions containing both components in appropriate concentrations. In such films, contacts between the two kinds of molecules take place in the whole volume of the film, unlike the bilayer OLED structure with very thin contact interface.

Kaplunov et al. [44] studied the PL spectra of the films containing blends of Zn(DFP-SAMQ)$_2$ with PTA. The spectra contain no intrinsic luminescence of zinc complex or PTA and exhibit only the exciplex band with maximum at 555 nm (figure 5, curve 4). Kaplunov et al. [45] studied the PL spectra of the films containing PTA, Zn(DFP-SAMQ)$_2$ and their blends in different ratios. For the films with a relatively low fraction of PTA where PTA:Zn(DFP-SAMQ)$_2$ = 0.5:1 and 1:1 (mass), the PL bands are close to that of Zn(DFP-SAMQ)$_2$ with $\lambda_{\text{max}}$ = 490 nm (intrinsic emission). For the films with a higher PTA fraction where PTA:Zn(DFP-SAMQ)$_2$ = 2.6:1 and 4:1 (mass), the exciplex PL band with $\lambda_{\text{max}}$ in the region of 560 nm is observed. This result shows that the exciplex PL can be observed for donor-acceptor blends with proper relation between components, which guarantees large amount and good quality of intermolecular donor-acceptor contacts.

4. Elimination of exciplex emission for the devices based on zinc complexes with amino-substituted ligands

4.1. Elimination of exciplex emission by introducing an intermediate layer between the hole-transporting and the emitting layers

To prove the exciplex origin of the long-wavelength EL, we have fabricated several control devices in which the long-wave EL bands are eliminated.

One of the methods for preventing exciplex emission is the insertion of an additional layer between the hole-transporting and electron-transporting materials [22,25-27]. CBP is considered as one of the materials appropriate for such layers [27,54,55]. We have fabricated two control devices with Zn(PSA-BTZ)$_2$ as emitting layer and CBP as the intermediate layer: ITO/PTA/NPD/CBP/Zn(PSA-BTZ)$_2$/Al:Ca (device D3) and ITO/PTA/CBP/Zn(PSA-
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Figure 2 shows the EL spectra of devices D3 and D4 (Figure 2a, curve 3 and Figure 2b, curve 2, respectively). In both cases, the EL spectra contain no wide band around 560 nm and exhibit only one band in the blue region with the maximum at 471 nm (device D3) and 469 nm (device D4), which may be attributed mainly to the intrinsic emission of the Zn(PSA-BTZ)₂ complex.

Similar to the devices based on Zn(PSA-BTZ)₂, the exciplex band can be eliminated by introducing the intermediate layer of CBP between NPD and Zn(POPS-BTZ)₂ or PTA and Zn(TSA-BTZ)₂. The EL spectrum of the device ITO/PTA/NPD/CBP/Zn(POPS-BTZ)₂/Al:Ca (device D9) is shown in Figure 4 (curve 2). The exciplex band in the region of 540 nm is absent, and only the intrinsic emission of Zn(POPS-BTZ)₂ at λ_max = 460 nm is observed. The EL spectrum of the device ITO/PTA/CBP/Zn(TSA-BTZ)₂/Al:Ca (device D12) is shown in Figure 3b (curve 2). The exciplex band in the region of 580 nm is absent, and only the intrinsic emission of Zn(TSA-BTZ)₂ at λ_max = 465 nm is observed.

4.2. The role of amino groups in exciplex formation

Exciplex can be formed at the solid interface between a hole-transporting layer and an electron-transporting layer, in case when there is a significant spatial overlap between the lowest unoccupied molecular orbitals (LUMOs) of the constituent species [56].

It should be noted that both NPD and PTA, as well as many other materials usually used to form the hole-transporting layer, are the derivatives of triarylamines. One may suppose that the interaction of the nitrogen atoms in the amino groups of the hole-transporting molecules and the amino groups of the zinc complexes (due to their spatial overlap) determines the exciplex formation in the studied systems. Evidence in favor of this supposition comes from our results on using other materials different from triarylamine derivatives for hole-transporting layers. Figure 2a, curve 4 shows the EL spectrum of device ITO/PEDOT:PSS/Zn(PSA-BTZ)₂/Al:Ca (device D5) where the hole-transporting layer is presented by PEDOT:PSS, a hole injecting and transporting material which does not contain nitrogen atoms at all. This spectrum does not contain a wide band around 560 nm and exhibits only one band with a maximum at 466 nm, which is close to the Zn(PSA-BTZ)₂ powder PL band (450 nm) and may be attributed mainly to the intrinsic emission of Zn(PSA-BTZ)₂ complex. One may suppose that the formation of exciplex in this case is suppressed by the absence of nitrogen atoms in the hole-transporting layers.

Commonly, the reason for preventing the exciplex emission by changing the hole-transporting material is argued to be the relation between the energy levels of the donor and acceptor molecules. Materials like CBP with low highest occupied molecular orbital (HOMO) energy level are considered as appropriate ones [22,25-27]. Really, the HOMO level of CBP is 6.1 to 6.3 eV below vacuum level [47,57,58], which is appreciably lower than that of NPD (5.2 to 5.7 eV) [58-60].

On the other hand, the highest occupied energy level of PEDOT:PSS is 5.2 eV below vacuum level [61], which does not differ from that of NPD. So, the fact that NPD produces exciplexes
with the studied complexes and CBP and PEDOT:PSS do not may be explained not only by positions of energy levels but also by other reasons. Good spatial overlap of donor and acceptor molecular orbitals seems to be one of the most important factors promoting the formation of exciplexes.

From this point of view, molecules with amino groups are most appropriate for exciplex formation because of high electron density at nitrogen atoms. Zinc complexes studied in the present work contain amino groups bonded to metal atom and produce exciplexes in pair with triarylamine molecules NPD and PTA. Note that the analogs of our complexes containing oxygen atom bonded to metal such as Mq$_3$, Znq$_2$, Zn(BTZ)$_2$ do not exhibit exciplexes in their EL spectra when triarylamine hole-transporting materials like NPD or TPD are used [1,3-6,47]. At the same time, the derivatives of Alq containing amino groups bonded to quinoline species exhibit EL exciplex bands for the devices with NPD [27].

5. The relation between intrinsic and exciplex bands in the devises containing NPD/Zn(TSA-BTZ)$_2$ interface

Some of the EL devices based on amino-substituted zinc complexes demonstrate the EL spectra with only exciplex bands, other demonstrate the intrinsic EL bands either. The relation between intrinsic and exciplex bands can be affected by different factors: materials of contacting layers [22], thicknesses of layers [17,29,30,31,62], applied voltage and current [20,63-64]. 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 hole-transporting layer and on the applied bias voltage were studied for the devises based on Zn(TSA-BTZ)$_2$ as an illustrative example.

![Figure 6](image_url)

**Figure 6.** Normalized EL spectra of ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca devices with different thicknesses of NPD layer: 8 nm (1), 15nm (2), 30 nm (3) and 45 nm (4). Spectra are measured at the same current 7.4 mA/cm$^2$ for all devices.
Figures 6 and 7 show the EL spectra of the devices ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca (device D6) with different thicknesses of 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.6). For thicknesses of 8, 15 and 30 nm, the exciplex band with maximum in the region of 590 nm is observed. Further increase in 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. Devices with 8 nm NPD layer thickness exhibit no intrinsic band in the EL spectra. Devices with 15, 30 and 45 nm NPD layer thickness exhibit intrinsic EL band in the region of 450-460 nm in addition to exciplex bands.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
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<tr>
<td>3.5</td>
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Figure 7. EL spectra of the devices ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca with different thicknesses of NPD layer: 8 nm (a), 15 nm (b), 30 nm (c) and 45 nm (d). The applied bias voltages and the currents through the device are given along with curve numbers.
Figure 7 shows the dependence of the EL spectra of Zn(TSA-BTZ)$_2$ based devices with different thicknesses of hole-transporting NPD layer on the applied bias voltages and corresponding currents through the device. With increasing voltage, maximum of the exciplex band shifts to lower wavelength by 5-8 nm, maximum of the intrinsic band practically does not change. The increasing voltage leads also to appearance of additional exciplex peak at 540 nm in the EL spectra of the devices with the NPD layer thicknesses of 15 and 30 nm (figure 7b,c).

Shift of exciplex bands maxima with change of the layer thicknesses and of the applied voltage may be due to plurality of excited states in the excited donor-acceptor complexes [28,51].

The relation of intensities of intrinsic and exciplex bands depends on applied bias voltage and corresponding currents. With increasing voltage, the intensity of the intrinsic band relative to the exciplex band increases. For the device with 30nm NPD layer thickness, the intrinsic band becomes more intense than the exciplex band at some voltages. Growth of the intrinsic band can be attributed to the shift of the carrier recombination zone from the NPD/Zn(TSA-BTZ)$_2$ interface to the bulk of the emitter layer and increasing number of holes injected into the emitter layer due to increasing electric field [29,63,65].

It should be noted that the intensity of electroluminescence depends on the number of recombining electrons and holes that is on 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 8](image_url)

**Figure 8.** Plot of relative intensities of the intrinsic EL band and that of exciplex band as a function of the current for the devices ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca with NPD layer thicknesses 30 nm (1, squares) and 45 nm (2, circles). Solid curves represent only guide to an eye.

Figure 8 shows the relation of the intensity of the intrinsic EL band (L$_{intr}$) to that of exciplex band (L$_{exc}$) for the devices with thicknesses of NPD layer 30 and 45 nm depending on
current. The intensity of the intrinsic band relative to that of the exciplex band increases with the increase in 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.

6. White OLEDs based on zinc complexes with amino-substituted ligands

The combination of narrow intrinsic band and wide exciplex band gives a very wide emission spread over the whole visible spectrum, which is a way to obtain white light emitting diodes [8,12,36,37].

For the novel zinc-chelate complexes of sulphanilamino-substituted ligands, the combination of narrow intrinsic band in blue region and wide exciplex band in yellow region can be observed for some devices with NPD as hole-transporting layer. For example, the device 1 based on Zn(PSA-BTZ)$_2$ gives the EL emission (Figure 2a, curve1) with the CIE chromaticity coordinates $x = 0.31$ and $y = 0.34$ which is close to that of the white light ($x = 0.33$, $y = 0.33$). Corresponding point on CIE color diagram (Figure 9) is marked by open circle.

![Figure 9](image_url)

Figure 9. The emission of the devices ITO/PTA/NPD/Zn(PSA-BTZ)$_2$/Al:Ca (open circle) and ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca with the NPD layer thickness of 30 nm (filled circles) on the CIE color diagram.

For the devices based on Zn(TSA-BTZ)$_2$, the presence of both intrinsic and exciplex emission bands in the EL spectra can be observed for the devices with appropriate NPD layer thickness. The EL spectra of the device ITO/PTA/NPD/Zn(TSA-BTZ)$_2$/Al:Ca with the NPD layer thickness of 30 nm exhibit both intrinsic and exciplex emission bands with the relation depending on bias voltages (figure 7c). The device emits nearly white light. The CIE color
coordinates \((x, y)\) corresponding to the emission spectra of the device at bias voltages 3.5, 4.0, 5.0 and 5.5 V are \((0.40, 0.38)\), \((0.37, 0.36)\), \((0.34, 0.33)\) and \((0.33, 0.33)\) respectively. Corresponding points on CIE color diagram (figure 9, filled circles) are close to the black body emission line between color temperatures 3500 and 6000 K.

As an example, Fig. 10 shows a photograph of a light-emitting diode based on the electroluminescent structure ITO/PTA/Zn(TSA-BTZ)/Al:Ca. The area of the luminescent surface is \(6\times6 \text{ mm}^2\) and the operation voltage is 6–8 V. The efficiency of such light-emitting diodes reaches 5–6 lm/W.

![Figure 10. Photograph of an organic light-emitting diode based on an ITO/PTA/Zn(TSA-BTZ)/Al:Ca electroluminescent structure.](image)

7. Conclusions

The novel zinc-chelate complexes of sulphanilamino-substituted quinolines and benzothiazoles are proper materials for OLEDs, with efficient exciplex emission giving rise to white OLEDs and OLEDs of different colors including blue, green, and yellow. Exciplex emission can also be observed in the PL spectra of the films containing blends of zinc complex and hole-transporting material. The main reason of effective exciplex formation 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 the molecules of the hole-transporting layer and hence magnify the possibility of exciplex forming. Material of the hole-transporting layer is crucial for the efficiency of exciplex formation. Triarylamine derivatives like NPD or PTA seem to be the most proper materials for exciplex formation. Exciplexes can be eliminated with only intrinsic bands remaining in the EL spectra when the hole-transporting layer is not a triarylamine derivative. This may be due not only to positions of energy levels but also to good spatial overlap and high electron density on amino groups of both zinc complex and
triarylamine derivatives. The relation between intrinsic and exciplex EL bands for the EL devices depends not only on the material of hole-transporting layer but also on the applied voltage. This may be due to the shift of the carrier recombination zone from the interface of hole-transporting and emitting layers to the bulk of the emitter layer.

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8. References


[65] Chen, T-R. Luminescence and electroluminescence of bis (2-(benzimidazol-2-yl) quinolinato) zinc. Exciplex formation and energy transfer in mixed film of bis (2-(benzimidazol-2-yl) quinolinato) zinc and N,N′-bis-(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine. Journal of Molecular Structure 2005; 737(1) 35-41.