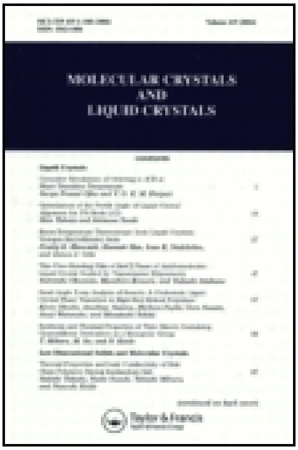

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Electroluminescent Devices Based on Novel Zinc Complexes of Sulphonylamino Substituted Heterocycles

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Electroluminescent Devices Based on Novel Zinc Complexes of Sulphonylamino Substituted Heterocycles

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The electroluminescent properties of some new materials based on novel zinc complexes of sulphonylamino substituted quinolines and 2-phenylbenzazoles are reported. The electroluminescent devices based on the new complexes exhibit a bright luminosity of green or nearly white color with good luminosity efficiency up to 25–30 cd/Å.

Keywords: organic electroluminescence; white light; zinc complexes

INTRODUCTION

One of the essential conditions of the effective work of an electroluminescent organic light-emitting diode is both the balanced injection of charges of both signs and the efficient charge transport to a luminescent layer. Now the number of the known hole-transporting substances is much higher than that of the electron transporting ones. Therefore, the search for new electron-transporting materials is actual [1,2].

Among low-molecular materials for electron-transporting layers, the chelate complexes of some metals (Al, Zn, Be) with heterocyclic ligands based on hydroxy-substituted quinolines and 2-phenylbenzazoles are most efficient. The most known and applied chelates are tris(8-hydroxyquinolate)aluminum, AlQ_3 and bis(2-(2-hydroxiphenyl)-benzothiazolate)zinc, $Zn(BTZ)_2$ [1–4]. Such a type of materials is characterized by high luminescence in the solid state and good electron

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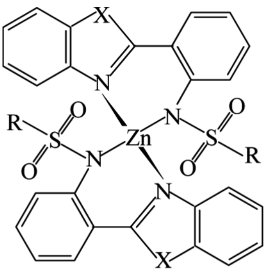
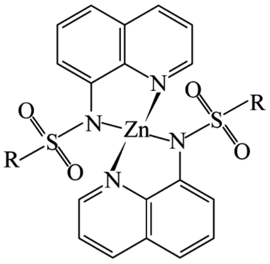
transporting and hole blocking properties [1–5]. However, the hydroxy substituted derivatives can be sensitive to chemical influences such as hydrolysis of metal-oxygen bonds by traces of oxygen and water, which results in the degradation of an electroluminescent device.

A possible way of the counteraction against such chemical influences is the replacement of oxygen atoms in the chelate cycle by nitrogen atoms of a sulfonylamine fragment. Ligands and metal complexes with sulfonylamine substituents are more stable due to the additional coordination of a metal atom to the oxygen atom of the sulfonic fragment. Due to their chemical nature, these substituents are also more stable with respect to oxidation and hydrolysis.

In view of this idea, we have synthesized some zinc complexes based on sulfonylamino derivatives of 2-phenylbenzazoles (complexes 1–7) and quinoline (complexes 8 and 9) [6,7]:



(1--7)



(8, 9)

where X–oxygen or sulfur atom, R–radicals:

(1) –X=O, R=$-C_6H_4CH_3$; (2) –X=S, R=$-C_6H_3F_2$ (3,5-difluorophenyl); (3) –X=S, R=$-C_6H_4CH_3$; (4) –X=S, R=$-C_{10}H_7$ (2-naphtyl); (5) –X=S, R=$-C_6H_5$; (6) –X=S, R=$-C_6H_4OC_{15}H_{31}$; (7) –X=S, R=$-CH_3$; (8) –R=$-C_6H_3F_2$ (3,5-difluorophenyl); (9) –R=$-CH_3$.

In this work, we present the results of studies of spectral properties of the complexes 1–9 and those of the electroluminescent devices prepared on the basis of these complexes.

EXPERIMENTAL

Zinc complexes were synthesized as described elsewhere [6–12]. The substances were characterized by elemental analysis, H-NMR, and IR spectra; TL-chromatography showed the absence of impurities.

Spectral properties. The absorption spectra of the complexes were measured on a Specord M40 spectrophotometer in the region of 200–900 nm. Samples were prepared by rubbing the substance on a quartz plate. The photoluminescence (PL) spectra of powders and films of the complexes and the electroluminescence (EL) spectra of the devices were measured on a plug-in spectrometer Ocean Optics PC1000 in the region of 350–800 nm. For the PL excitation, a light-emitting diode with emission at 370 nm was used. For complexes, the PL quantum yield was evaluated by the comparison with that of AlQ_3, for which the quantum yield is 32% [13] with the use of the apparatus described elsewhere [9].

Preparation of electroluminescence devices. Glass supports covered with patterned indium—tin oxide (ITO) were used as anodes. Either NPD (NPB) [14,15] or the triphenylamine oligomer PTA [16] were deposited on the anode as hole-transporting layers. PTA was deposited by spin casting from a solution in toluene, and NPD was deposited by evaporation *in vacuo*. An emitting layer consisting of one of the complexes under study was deposited on the transporting layer by evaporation *in vacuo*. The preparation of the device was completed by the vacuum sputtering of a metallic cathode of Al:Ca alloy (~20:1 wt/wt). Parts of the organic layer not covered with a metal were used for measuring its PL spectra. 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 $\sim 4\,\mathrm{mm}^2$. Methods of measuring the voltammetric characteristics and EL brightness of the devices are described elsewhere [7,11].

RESULTS AND DISCUSSION

Figure 1 shows the absorption and PL spectra of powders of two complexes $Zn(PSA\text{-}BTZ)_2$ (complex 5 of benzazole series, X = S, R = C_6H_5) and $Zn(DFP\text{-}SAMQ)_2$ (complex 8 of quinoline series,

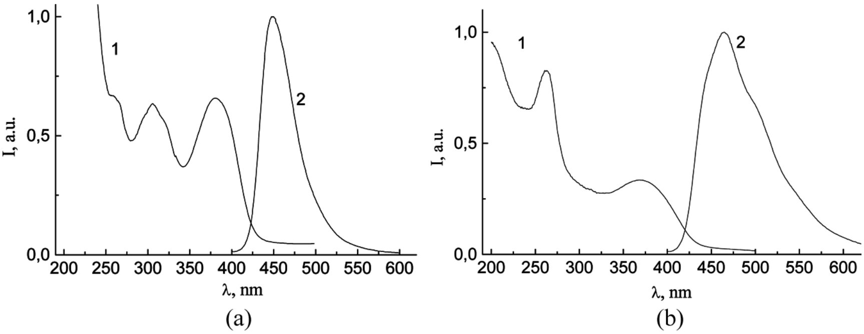


FIGURE 1 Absorption (1) and PL (2) spectra of powders for $Zn(PSA\text{-}BTZ)_2$ (a) and $Zn(DFP\text{-}SAMQ)_2$ (b).

R = difluorophenil) as typical of the materials studied. The parameters of the absorption and PL spectra for complexes (1) to (9) are listed in Table 1. All the complexes are characterized by the absorption bands below 400 nm with the most long-wavelength band in the region of 370–390 nm. Maxima of PL bands for all the complexes are in the region of 415–500 nm. Half-widths of the PL bands are about 50–60 nm for benzazole complexes (1) to (7) and about 90 nm for quinoline complexes (8) and (9). Similar parameters of PL bands were observed for powders and films of the complexes. The PL quantum yields determined for powder samples of the complexes are also listed in Table 1. The quantum yields of most of the complexes are comparable or much higher than that of AlQ_3.

To study the electroluminescent properties of the new complexes, we prepared electroluminescent devices of the structure ITO/HTL/ETL/Al:Ca, where HTL is a hole transporting layer of NPD or PTA, and ETL is an emitting layer of one of the two complexes $Zn(PSA\text{-}BTZ)_2$ or $Zn(DFP\text{-}SAMQ)_2$.

Figure 2 shows the current-voltage and brightness-voltage curves for the device ITO/PTA/$Zn(DFP\text{-}SAMQ)_2$/Al:Ca which is typical of all the devices under investigation. Both curves have a non-linear diode-type shape and nearly coincide on the appropriate scale which is an evidence of no leakage currents. The turn-on voltage of the device is 4 V. Brightness of about 1500 cd/m^2 is attained at a voltage of 6.1 V and a current density of about 5–6 mA/cm^2, which corresponds to a luminosity efficiency of 25–30 cd/Å, being a rather good result [1,2].

The most interesting results were obtained when studying the EL spectra of the devices. It is well-known that the EL spectra of most of the organic materials are similar to their PL spectra, which is explained by the fact that the energy levels involved in EL and PL processes are the same [1–5]. The opposite situation is observed for

TABLE 1 Spectral Properties of the Complexes Under Study

Complex	Absorption, λ_{max}, nm	PL, $\lambda_{max}(\Delta\lambda)$, nm	PL QY, %
(1) X = O, R = $-C_6H_4CH_3$	375	415 (50)	30
(2) X = S, R = $-C_6H_3F_2$	390	430 (50)	10
(3) X = S, R = $-C_6H_4CH_3$;	390	441 (60)	50
(4) X = S, R = $-C_{10}H_7$	390	445 (50)	30
(5) X = S, R = $-C_6H_5$	390	448 (50)	50
(6) X = S, R = $-C_6H_4OC_{15}H_{31}$	390	450 (50)	40
(7) X = S, R = $-CH_3$	385	463 (60)	22
(8) R = $-C_6H_3F_2$	370	465 (90)	90
(9) R = $-CH_3$	382	500 (90)	20

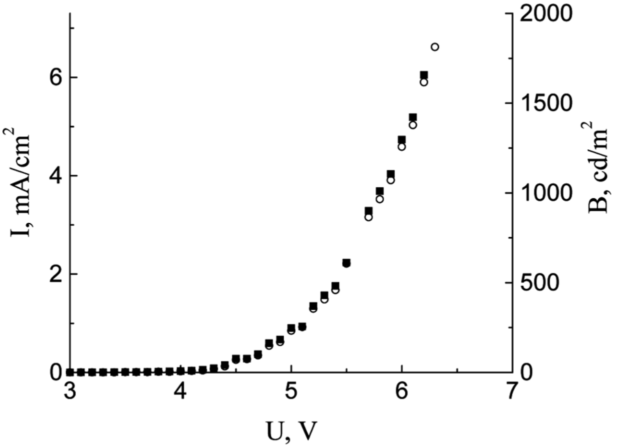
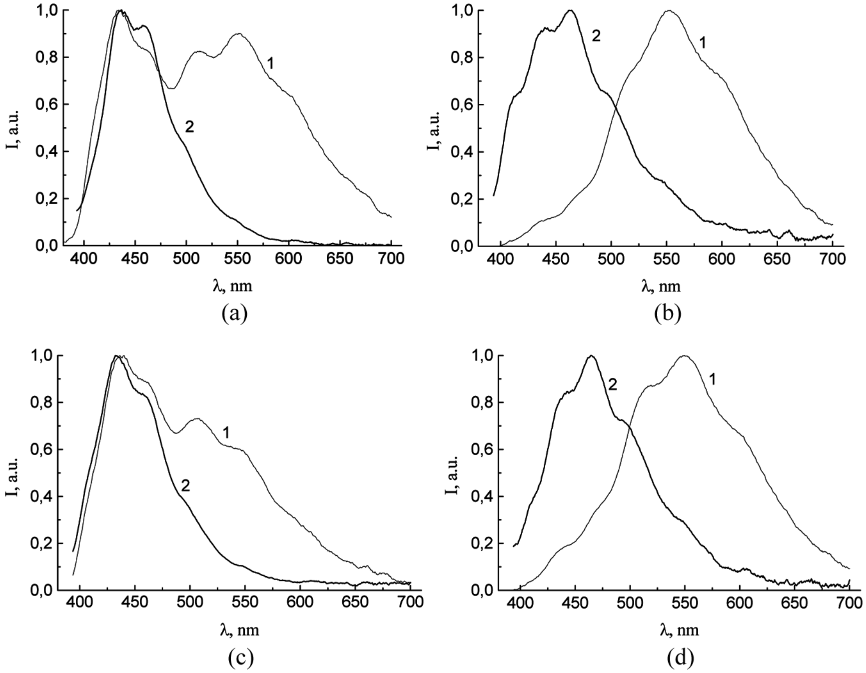


FIGURE 2 Current-voltage (open circles) and brightness-voltage (solid squares) curves for an ITO/PTA/Zn(DFP-SAMQ)$_2$/Al:Ca device.

our devices: the EL spectra significantly differ from the PL spectra of the organic components.

Figure 3 shows the EL spectra of the devices based on Zn(PSA-BTZ)$_2$ or Zn(DFP-SAMQ)$_2$ complexes with two hole-transporting materials, NPD and PTA. The PL spectra of organic layers of the electroluminescent structure are shown as well. In the EL spectra of the devices based on NPD as the hole-transporting material (Figs. 3a and 3c), the component around 450 nm may be attributed to the intrinsic electronic transitions of the zinc complex (with a possible contribution of that of NPD). This component coincides with the PL spectrum of the sample. Besides this intrinsic band, the additional wide EL band in the region of 500–650 nm is observed. While PL is excited in the film bulk, EL arises in the interface region between the hole-transporting and electron-transporting layers. The additional long-wavelength EL band may be due to some interactions in this interface region, probably to the formation of an exciplex. This means that a molecule of ETL containing an additional electron on its excited energy level and a molecule of HTL containing a hole on its main energy level can form an excited complex (exciplex), and the recombination of the electron and the hole results in the long-wave EL band, while the intrinsic blue EL band is due to the recombination of an electron and a hole on one molecule of ETL. A similar effect of the formation of an additional long-wavelength EL band was observed for the electroluminescent device based on NPD and a boron hydroxyphenylpyridine complex and was attributed to exciplex emissions [17].



(a) (b) (c) (d)

FIGURE 3 EL (1) and PL (2) spectra of the electroluminescent structures: (a) ITO/NPD/Zn(PSA-BTZ)$_2$/Al:Ca, (b) ITO/PTA/Zn(PSA-BTZ)$_2$/Al:Ca, (c) ITO/NPD/Zn(DFP-SAMQ)$_2$/Al:Ca, (d) ITO/PTA/Zn(DFP-SAMQ)$_2$/Al:Ca.

Due to the large width of the EL spectrum extending from the blue to the red spectral region, the emission of a device based on Zn(PSA-BTZ)$_2$ and NPD is nearly white. The CIE color coordinates are $x = 0.30$, $y = 0.34$ which are rather close to that of pure white ($x = 0.33$, $y = 0.33$). For the EL spectrum of a device based on Zn(DFP-SAMQ)$_2$ and NPD, the color coordinates are $x = 0.24$, $y = 0.28$.

In the EL spectra of the devices based on PTA as a hole-transporting material (Figs. 3b and 3d), the component around 450 nm is not observed, while the PL spectra of the whole electroluminescent structure exhibit such a band. The EL spectra consist only of the wide "exciplex" band with a maximum around 550 nm. Probably, PTA is a more favorable material for the exciplex formation. Color of the EL for the devices based on PTA is yellow-green with the CIE color coordinates $x = 0.39$, $y = 0.49$ for a Zn(PSA-BTZ)$_2$-based device and $x = 0.36$, $y = 0.47$ for a Zn(DFP-SAMQ)$_2$-based device.

In summary, we have synthesized chelate metal complexes of a new type based on sulfonylamino derivatives of quinoline and

2-phenylbenzazoles and have studied their electroluminescent properties. The electroluminescent devices based on these complexes exhibit a high luminosity efficiency. The EL spectra of the devices based on these complexes exhibit the additional wide band probably due to the exciplex emission. Some of the devices emit nearly white light.

REFERENCES

[1] Mitschke, U. & Bauerle, P. (2000). *J. Mater. Chem.*, *10*, 1471.

[2] Shirota, Y. & Kageyama, H. (2007). *Chem. Rev.*, *107*, 953.

[3] Chen, C. H. & Shi, J. (1998). *Coord. Chem. Rev.*, *171*, 161.

[4] Hamada, Y., Sano, T., Fujii, H., Nishio, Y., Takahashi, H., & Shibata, K. (1996). *Jpn. J. Appl. Phys.*, *35*, L1339.

[5] Sano, T., Nishio, Y., Hamada, Y., Takahashi, H., Uzuki, T., & Shibata, K. (2000). *J. Mater. Chem.*, *10*, 157.

[6] Kaplunov, M. G., Yakushchenko, I. K., Krasnikova, S. S., Shamaev, S. N., Pivovarov, A. P., & Balashova, I. O. (2008). *High Energy Chemistry*, *42*(4), 55.

[7] Krasnikova, S. S., Yakushchenko I. K., Shamaev, S. N., & Kaplunov, M. G. (2007). *Mol. Cryst. Liq. Cryst.*, *468*, 87.

[8] Kaplunov, M. G., Krasnikova, S. S., Yakushchenko, I. K., Ermakov, O. N., & Stakharny, S. A. (2004). *Mater. Science-Poland*, *22*, 571.

[9] Pivovarov, A. P., Kaplunov, M. G., Yakushchenko, I. K., Belov, M. Yu., Nikolaeva, G. V., & Efimov, O. N. (2002). *Russian Chem. Bull.*, *51*, 67.

[10] Pivovarov, A. P., Kaplunov, M. G., Efimov, O. N., Yakushchenko, I. K., & Belov, M. Yu. (2001). *Mol. Cryst. Liq. Cryst.*, *361*, 263.

[11] Kaplunov, M. G., Yakushchenko, I. K., Krasnikova, S. S., Shamaev, S. N., Pivovarov, A. P., & Efimov, O. N. (2004). *Russian Chem. Bull.*, *53*, 2148.

[12] Kaplunov, M. G., Krasnikova, S. S., Yakushchenko, I. K., Shamaev, S. N., Pivovarov, A. P., Efimov, O. N., Ermakov, O. N., & Stakharny, S. A. (2005). *Mol. Cryst. Liq. Cryst.*, *426*, 287.

[13] Garbuzov, D. Z., Bulovic, V., Burrows, P. E., & Forrest, S. R. (1996). *Chem. Phys. Lett.*, *249*, 433.

[14] Van Slyke, S. A., Chen, C. H., & Tang, C. W. (1966). *Appl. Phys. Lett.*, *69*, 2160.

[15] Uekawaa, M., Miyamoto, Y., Ikeda, H., Kaifu, K., Ichi, T., & Nakaya, T. (1999). *Thin Solid Films*, *352*, 185.

[16] Yakushchenko, I. K., Kaplunov, M. G., Efimov, O. N., Belov, M. Yu., & Shamaev, S. N. (1999). *Phys. Chem. Chem. Phys.*, *1*, 1783.

[17] Liu, Y., Guo, J., Zhang, H., & Wang, Y. (2002). *Angew. Chem. Int. Ed.*, *41*, 182.