New electroluminescent materials based on chelate zinc complexes

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Three new chelate zinc complexes with azomethine groups characterized by luminescence in the visible spectral region were synthesized: bis(N-(2-oxybenzylidene)cyclohexylamine)zinc,bis(N-(2-oxybenzylidene)-4-tert-butylaniline)zinc, and N,N'-bis(oxybenzylidene)-1,2-phenylenediaminezinc. Their spectral properties were studied. Based on these complexes, weprepared electroluminescence devices giving an intense emission in the blue, green, and redspectral regions.

Key words: electroluminescence, photoluminescence, metal complexes.

It is of interest to study electroluminescence of organic materials for both understanding fundamental processes in organic solids and from the viewpoint of possible practical applications.¹⁻⁵ Despite success achieved in this area, the problem of search for new efficient materials and structures for organic electroluminescence devices remains very urgent. Active electroluminescent materials (ELM) should possess an efficient luminescence and good transport properties. Among these materials, chelate metal complexes, for example well-known aluminum 8-hydroxyquinolate,¹⁻⁵ play an important role. Electroluminescent materials based on zinc complexes were also obtained. $^{6-10}$ In particular, the zinc complexes containing an azomethine group -CH=N-R (R is an alkyl group) were proposed. They are characterized by luminescence in the blue spectral region. 6,7 In this work, we synthesized three new ELM based on the chelate zinc complexes with azomethine groups: bis(N-(2-oxybenzylidene)cyclohexylamine)zinc(II) (Zn(OBCG)₂), bis(N-(2-oxybenzylidene)-4-tert-butylaniline)zinc(II) (Zn(OBBA)₂), and N, N'-bis(oxybenzylidene)-1,2-phenylenediaminezinc(II) (Zn(OBPDA)). They luminesce in the blue and green spectral regions.

Introduction of different substituents to nitrogen atoms or their linking by bridges makes it possible to control the position of maxima in absorption and luminescence spectra due to changes in the electron density and conjugation length.

Based on the synthesized complexes, we prepared electroluminescence devices and studied their properties. We also studied a device with an active layer as a solid solution of Nile Red (NR) in $Zn(OBBA)_2$ in a weight ratio of ~0.005 : 1, which is characterized by the red luminescence.^{11,12} As a result, the electroluminescent systems based on the zinc chelates emitting intensely in the blue, green, and red spectral regions were obtained.



Experimental

Synthesis of the zinc complexes. Ligands N-2-hydroxybenzylidenecyclohexylamine, N-2-hydroxybenzylidene-4-*tert*butylaniline, and N,N'-bis(2-hydroxybenzylidene)-1,2-phe-

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nylenediamine were prepared by the reactions of salicylaldehyde with cyclohexylamine, 4-*tert*-butylaniline, or 1,2-phenylenediamine, respectively. Then a complex was synthesized by the reaction of the corresponding ligand with zinc chloride in an aqueous solution containing potassium hydroxide.

Spectral properties were measured according to a procedure described earlier.¹¹ Samples for measuring absorption and photoluminescence spectra were prepared as films deposited on a quartz support by the same method as those for electroluminescence devices. IR spectra were measured for KBr pellets on a Perkin—Elmer Spectrum BX FTIR spectrometer.

<u>Complex Zn(OBCG)</u>₂, m.p. 196–197 °C. Found (%): C, 66.32; H, 6.83; Zn, 13.91. $C_{26}H_{32}N_2O_2Zn$. Calculated (%): C, 66.45; H, 6.86; Zn, 13.91. IR, v/cm⁻¹: 3086 v.w, 3043 v.w, 3022 v.w, 2933 m, 2855 w, 1614 v.s, 1538 s, 1466 s, 1447 s, 1410 m, 1363 v.w, 1340 m, 1320 m, 1307 w, 1244 v.w, 1191 m, 1149 m, 1126 w, 1075 m, 1032 w, 988 v.w, 972 v.w, 921 w, 889 w, 852 w, 814 w, 776 w, 757 m, 740 m, 663 w, 611 w, 572 v.w, 550 w, 498 w, 456 w, 422 v.w.

<u>Complex Zn(OBBA)</u>₂, m.p. 257–258 °C. Found (%): C, 78.80; H, 6.35; N, 4.93. $C_{34}H_{36}N_2O_2Zn$. Calculated (%): C, 71.64; H, 6.37; N, 4.92. IR, v/cm⁻¹: 3070 w, 3060 w, 3025 w, 2962 m, 2929 v.w, 2866 w, 1610 v.s, 1588 v.s, 1532 s, 1509 m, 1462 s, 1441 s, 1421 v.w, 1401 w, 1389 m, 1362 w, 1354 w, 1327 m, 1310 w, 1268 v.w, 1255 v.w, 1228 v.w, 1194 w, 1177 s, 1150 s, 1127 w, 1110 w, 1030 w, 1051 w, 988 w, 944 v.w, 928 w, 911 v.w, 868 w, 839 m, 788 w, 754 m, 742 w, 621 w, 596 m, 556 w, 545 v.w, 521 w, 501 w, 479 w, 436 v.w.

<u>Complex Zn(OBPDA)</u>, m.p. 354–355 °C. Found (%): C, 63.44; H, 3.91; Zn, 17.10. $C_{20}H_{14}N_2O_2Zn$. Calculated (%): C, 63.26; H, 3.72; Zn, 17.22. IR, v/cm⁻¹: 3073 w, 3014 w, 2923 w, 2854 w, 1617 v.s, 1587 s, 1531 s, 1463 s, 1446 m, 1387 m, 1351 w, 1326 m, 1245 w, 1230 v.w, 1181 s, 1153 s, 1127 m, 1109 v.w, 1049 v.w, 1032 w, 970 w, 919 m, 854 v.w, 844 v.w, 799 w, 741 s, 602 w, 551 v.w, 533 m, 511 w, 492 w, 438 v.w.

Preparation of electroluminescence devices. Glass supports covered with transparent conducting indium-tin oxide In₂O₃-SnO₂ (indium-tin oxide, ITO) were used as anodes with a resistance of ~ 20 Ohm cm⁻². A hole-transporting layer (mixture of triphenylamine oligomers (PTA))¹³ was deposited on the anode (by pouring from a solution in benzene), or N, N'-diphenyl-N, N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine $(TPD)^{1-5}$ was deposited on the anode 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 emitting layer, being a solid solution of NR in Zn(OBBA)₂, was deposited only on PTA from a solution containing NR and Zn(OBBA)₂ in the corresponding ratios.¹¹ The preparation of the device was completed by vacuum sputtering of a metallic cathode of Al or a Mg-Ag alloy (10 : 1 wt/wt). 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 $\sim 5 \text{ mm}^2$.

To measure the voltammetric characteristics, an enhanced voltage from a PI-50 computer-controlled potentiostat was applied to a sample, and the current value from the potentiostat entered a computer through an analog-to-digital converter. The brightness of EL of the device was measured with a FEU-39a photomultiplier, taking into account the geometry of the setup and passport sensitivity of the FEU.

Results and Discussion

The absorption and photoluminescence (PL) spectra of vacuum deposited films of the complexes under study are presented in Fig. 1. The absorption spectra contain bands with maxima at 226, 245, 280, and 376 nm (Zn(OBCG)₂); 235, 311, and 410 nm (Zn(OBBA)₂); 243, 297, 387, and 450 nm (Zn(OBPDA)). The maximum of the longest-wave absorption band shifts to longer wavelengths in the series Zn(OBCG)₂, Zn(OBBA)₂, and Zn(OBPDA). The PL spectra were measured upon excitation with spectral lines corresponding to the longwave absorption bands: $\lambda_{exc} = 390$ (Zn(OBCG)₂), 406 (Zn(OBBA)₂), and 460 nm (Zn(OBPDA)). The PL spectra of the complexes under study exhibit broad (halfwidth ~100 nm) bands with maxima at 453, 510, and 565 nm, respectively. The maxima of the PL bands and the



Fig. 1. Absorption (1) and luminescence (2) spectra of the complexes under study: a, Zn(OBCG)₂; b, Zn(OBBA)₂ (dotted curve shows the luminescence spectrum of the Zn(OBBA)₂ + 0.5% NR system); c, Zn(OBPDA).

Complex	Color of PL	Absorbance, λ_{max}/nm	PL	EL	Brightness*/cd m ⁻²	Efficiency*
			$\lambda_{\max}(\Delta\lambda)/nm$		(under voltage/V)	/cd A ⁻¹
$Zn(OBCG)_2$	Blue	376	453 (87)	450 (75)	120 (8.4)	1.4
$Zn(OBBA)_2$	Green	406	510 (115)	520 (112)	360 (12.7)	15
Zn(OBPDA)	Yellow-green	387, 450	565 (95)	570 (100)	360 (8.5)	1.7
$Zn(OBBA)_2 + NR$	Red	406, 525	625 (50)	625-650	_	_

Table 1. Data on the absorbance, photoluminescence (PL), and electroluminescence (EL) of the synthesized complexes and related devices

* For devices with the PTA transport layer and Mg—Ag cathode.

maximum of the longest-wave absorption band shift toward longer waves in the series $Zn(OBCG)_2$, $Zn(OBBA)_2$, and Zn(OBPDA). According to our estimate, the quantum yield of photoluminescence of the vacuum deposited films is 20–25 ($Zn(OBCG)_2$), 7–10 ($Zn(OBBA)_2$), and 1–2% (Zn(OBPDA)). For the first two complexes, the quantum yield is comparable with that for aluminum 8-hydroxyquinolate widely used in electroluminescence devices. According to data of independent authors, the PL quantum yield of Alq₃ ranges from 8–10 to 32%.¹⁴ The film containing 0.5% NR in $Zn(OBBA)_2$ is characterized by a PL band in the red spectral region with a maximum at 625 nm, which is related to the transfer of an electron excitation energy from $Zn(OBBA)_2$ molecules to NR molecules.^{11,12}

The electroluminescence devices prepared by the above-described procedure emit a visible light when an electric voltage is fed directly. The electroluminescence spectra are close to the photoluminescence spectra. The voltammetric and volt-brightness characteristics typical of the electroluminescent structures under study are presented in Fig. 2. Both characteristics are of diode character: the current increases sharply beginning from some threshold, and the brightness is approximately proportional to the current. On going from Al to the Mg-Ag alloy as a cathode, the threshold of light appearance decreases from 10-12 to 5-7 V, and the brightness increases sharply (by two orders of magnitude). The replacement of TPD by PTA does not substantially change the electric and light parameters; however, the durability of the device can increase sufficiently due to a higher glass transition temperature of PTA.¹³

The data on the absorbance, photoluminescence, and electroluminescence of the synthesized complexes and related devices are presented in Table 1. The brightness values given in Table 1 correspond to maximally possible voltages under which the devices can operate in a stable regime for several minutes. At higher voltages, the device is rapidly destroyed, probably, due to overheating. The efficiency of the device (see Table 1) is determined as a luminous intensity per current unit and corresponds to maximum brightness values. The



Fig. 2. Voltammetric (solid curve) and volt-brightness (dotted curve) characteristics of the electroluminescence device with the ITO/PTA/Zn(OBBA)₂/Mg-Ag structure; j is current strength, B is brightness, and U is voltage.

brightness and efficiency are presented for devices containing PTA as a hole-transporting layer and the Mg—Ag alloy as a cathode. Note that the efficiencies determined by us are higher than those for similar zinc complexes with azomethine groups (0.17 cd A^{-1} for an analog of Zn(OBCG)₂ and Zn(OBBA)₂ and 1.58 cd A^{-1} for an analog of Zn(OBPDA)),⁷ while for the ITO/PTA/Zn(OBBA)₂/Mg—Ag structure they are much higher than those for a series of other known devices based on zinc complexes (1.3—3.23 cd A^{-1}).^{7,8} The device containing a Zn(OBBA)₂ layer doped with NR manifests an electroluminescence in the red region; however, no quantitative parameters were measured for this device.

Thus, the electroluminescent systems based on new zinc chelates were obtained. They give an intense emission in the blue, green, and red spectral regions.

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