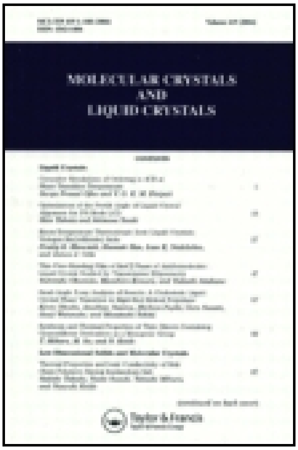

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New Organic Electroluminescent Materials

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New Organic Electroluminescent Materials

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Spectral and electric properties of five new materials for electroluminescent devices are described including materials for emitting layers and a high-T_g hole-transporting material.

Keywords: new materials; organic electroluminescence; photoluminescence

The study of organic electroluminescent (EL) materials is now a rapidly developing field of science due to promising practical applications [1,2]. In spite of impressing achievements of the last decade, the problem of searching for new effective luminescent materials of different emission colors is still actual. Another important task in the design of organic EL devices is the improvement of their thermal stability to prevent the degradation due to morphological changes in amorphous organic layers near the glass transition temperature (T_g). Therefore, materials with high T_g are urgently needed for organic EL devices.

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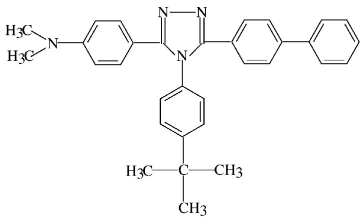
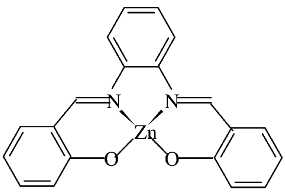
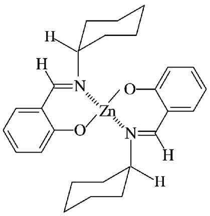
In the present work, we report the results of studies of spectral and electroluminescent properties of some new materials. The chemical structures of the materials under investigation are as follows:



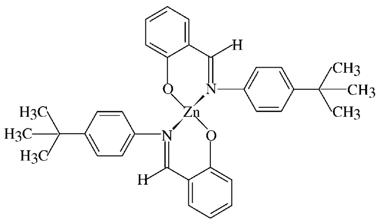
DA-BuTAZ



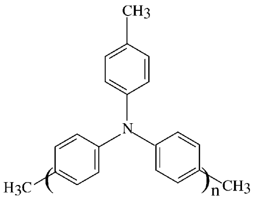
Zn(OB-PDA)



Zn(OBCG)$_2$



Zn(OBBA)$_2$



PTA

3-(4-dimethylaminophenyl)-4-(4′-*tert*-butylphenyl)-5-diphenyl-1,2,4-triazole, DA-BuTAZ, is a perspective 1,2,4-triazole derivative for blue emitting layers [3].

In [4], certain zinc complexes containing azomethine group -CH=N-R (were R stands for an alkyl group) and characterized by blue electroluminescence had been proposed. Here, we have synthesized three new electroluminescent materials based on zinc chelate complexes with azomethine groups characterized by electroluminescence in blue and green spectral regions, namely bis(N-(2-oxybenzylidene) cyclohexylamine)-zinc, Zn(OBCG)$_2$, N,N′-bis(2′-oxybenzylidene)-1,2-phenylenediamine-zinc, Zn(OBPDA) and bis(N-2-oxybenzylidene)-4-*tert*-butylaniline)-zinc, Zn(OBBA)$_2$ [5]. The addition of different substitutes at nitrogen atoms or bridges between them gives a tool to change the positions of absorption and luminescence spectral maxima due to changes in electron density and conjugation length.

We have also proposed a novel high-T_g oligomeric material (PTA) for hole-transporting layers (HTL) in EL devices based on triphenylamine.

Dimeric triphenylamine is a well-known hole-transporting material N,N′-diphenyl-N′N′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD) which shows excellent hole injection and transport capability with good electron-blocking capability at the HTL boundary but is not very stable due to its low T_g [6]. Oligomers of triphenylamine with the oligomerization number $n = 2$-5 were shown to have good hole-transporting characteristics. For these materials, T_g is shown to increase with n from 60°C for TPD to 140°C for an oligomer with $n = 5$ [6]. PTA is a mixture of triphenylamine oligomers of the general formula shown above with the oligomerization number $n = 7$–11 and is characterized by T_g as high as 185°C [3].

EXPERIMENTAL PROCEDURE

The synthesis of the materials studied was described elsewhere [3,5]. TPD was an Aldrich commercial product. The electroluminescent devices in our study were of the four-layered structure ITO/HTL/EML/M, where ITO is a transparent anode of In_2O_3:SnO_2 on a glass substrate, HTL is a hole-transporting layer, EML is an emitting layer and M is a metallic cathode of Al or Mg:Ag alloy. The HTLs were prepared by spin casting of PTA or vacuum evaporation of TPD. EMLs and metal cathodes were prepared by vacuum evaporation at a base pressure of about $5 \cdot 10^{-6}$ Torr.

The current-voltage and brightness-voltage characteristics of the EL devices were measured simultaneously with a computer-controlled potentiostat PI-50 and a calibrated photomultiplier or with a Hewlett-Packard semiconductor parameter analyzer HP4155A and a Si photodiode. The technique for measuring the absorption and photoluminescence (PL) spectra and PL quantum yields is described elsewhere [7].

RESULTS AND DISCUSSION

Figure 1 shows the absorption and photoluminescence (PL) spectra for the evaporated films of the materials studied. For the zinc chelate complexes, the maximum of the longest-wave absorption band shifts to longer waves in the array $Zn(OBCG)_2$, $Zn(OBBA)_2$, Zn(OBPDA). In the PL spectra, the broad (a half-width of about 100 nm) bands with maxima at 453, 510, and 565 nm, respectively, are shifted to longer waves in the same array. For DA-BuTAZ films, the PL maximum is observed at about 455 nm. We have measured the PL quantum yield for DA-BuTAZ and PTA in benzene solutions and have obtained it to be about 90% and 70%, respectively. We estimated the PL quantum

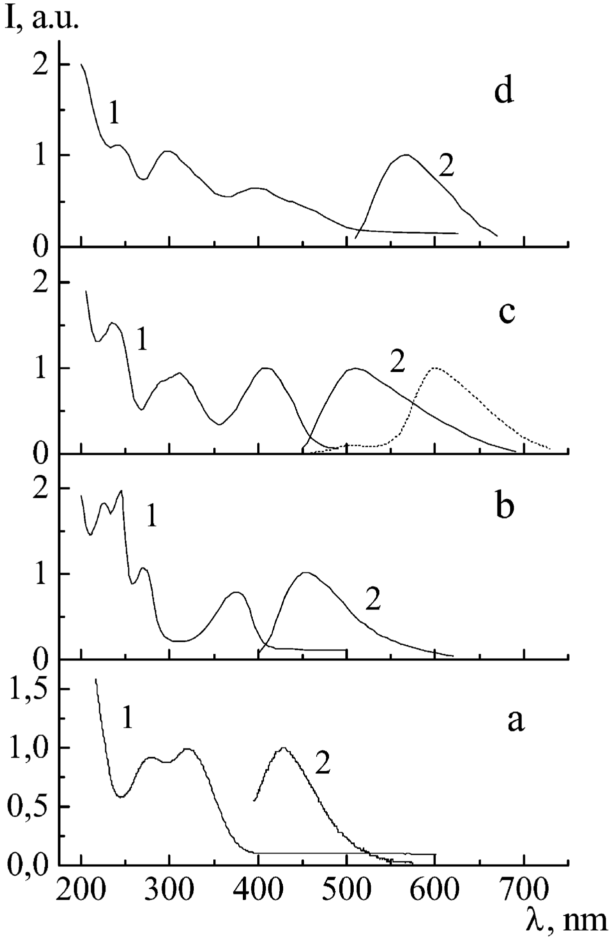


FIGURE 1 Absorption (1) and photoluminescence (2) spectra of the materials studied. a – DA-BuTAZ, b – Zn(OBPDA), c – Zn(OBBA)$_2$ (dashed curve – PL of the film containing 0.5% of Nile Red), d – Zn(OBCG)$_2$.

yields for the evaporated films of zinc complexes to be 20–25% for Zn(OBCG)$_2$, 7–10 % for Zn(OBBA)$_2$, and 1–2% for Zn(OBPDA). With the exception of the last complex, the quantum yields are comparable or higher than those of the well-known tris-8-oxyquinolate aluminum Alq$_3$ whose PL quantum yield is from 8–10 to 32%, according to different authors [8]. The film containing 0.5% of Nile Red (NR) in Zn(OBBA)$_2$ is characterized by a PL band in the red spectral region with the maximum at 625 nm and the quantum yield of about 100%

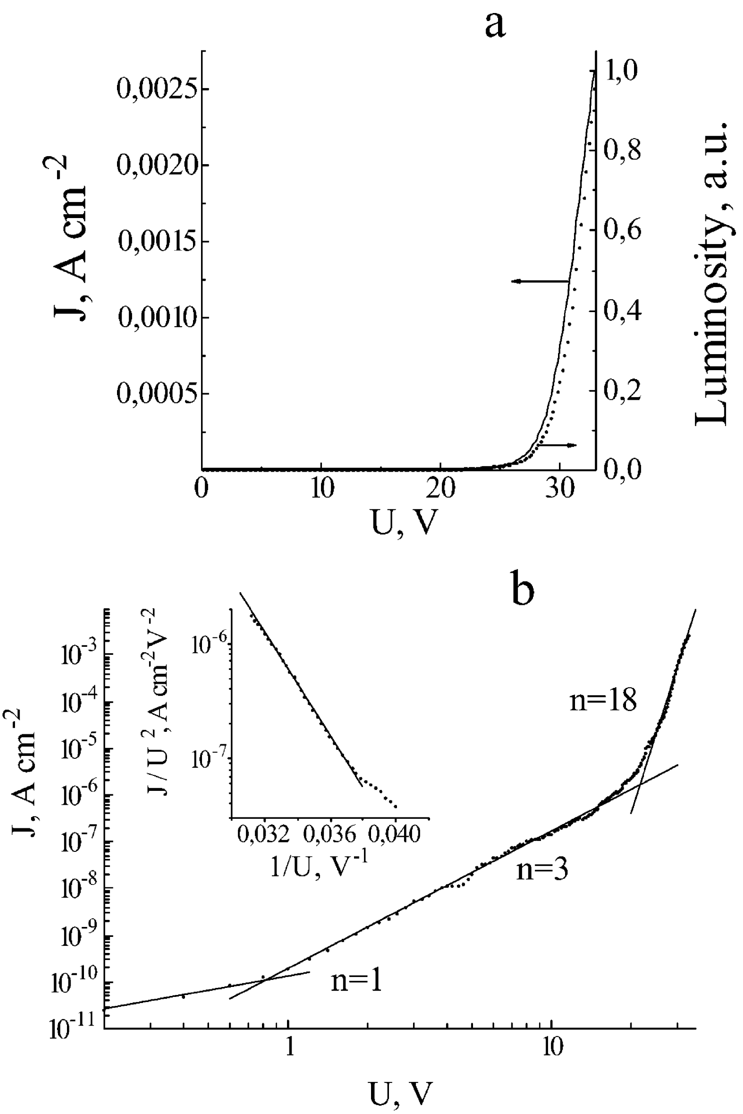


FIGURE 2 a – typical current-voltage and brightness-voltage characteristics of the EL device ITO/TPD/DA-BuTAZ/Al; b – the current-voltage curve of the same device on a double logarithmic scale; the insert shows a part of this curve in the Fowler-Nordheim coordinates J/U^2 vs. $1/U$.

TABLE 1 Absorption, Photoluminescence (PL), and Electroluminescence (EL) of the Materials Studied

	Color	Absorption, $\lambda_{\max}$, nm	PL, $\lambda_{\max}(\Delta\lambda)$, nm	PL QY,%	EL, $\lambda_{\max}$ ($\Delta\lambda$), nm	Brightness, cd/m^2 (at voltage, V)	EL efficiency, cd/A
DA-BuTAZ	Blue	320	455 (70)	>90	451 (70)	120 (12,8)	24
Zn(OBCG)$_2$	Blue	376	453 (87)	20–25	450 (75)	120 (8,4)	1,4
Zn(OBBA)$_2$	Green	406	510 (115)	7–10	520 (112)	360 (12,7)	15
Zn(OBPDA)	Yellow-green	387–415	565 (95)	1–2	560–580	360 (8,5)	1,7
Zn(OBBA)$_2$ + NR	Red	406; 525	625 (50)	~100	625–650	280 (20)	0,1
PTA	Blue	370	420 (120) 480 (sh)	~70			

which is due to the electron excitation energy transfer from Zn(OBBA)$_2$ molecules to NR molecules [7,9]. The spectral properties of the materials studied are summarized in Table 1.

The typical current-voltage and brightness-voltage characteristics of the devices studied are shown in Figure 2a for the ITO/TPD/DA-BuTAZ/Al structure. A change of TPD with PTA does not principally change the electric and luminous properties, but systems with PTA are more stable. The change of the Al cathode with Mg:Ag alloy gives a sufficient increase in luminosity (about two orders of magnitude) and a shift of the light appearance threshold to lower voltages (for DA-BuTAZ, it occurs down to 8–10 V). The EL properties of the materials studied are given in Table 1 for the ITO/PTA/EML/Mg:Ag structure.

Figure 2b shows current density J vs voltage U on a double logarithmic scale. Three regions can be seen at the current-voltage curve. At low voltages (less than 1 V), the current is proportional to the voltage, which is the usual Ohmic behavior. Beyond the Ohmic region up to the light appearance threshold, the dependence of current on voltage follows a power low ($J \sim U^{\mathbf{n}}$). Such a behavior is characteristic of space charge limited currents with regard for traps and, indeed, had been observed in EL devices based on Alq$_3$ and polymers with $\boldsymbol{n}$ changing from 2 to about 10 [10,11]. The third region (beyond the light appearance threshold) may be characterized by a power law with very high exponent ($\mathbf{n} = 18$–30) which is higher than usually observed quantities [10,11]. An alternative explanation of this region is the injection limitation of current, for example by the Fowler-Nordheim tunnelling mechanism which was shown to be appropriate for some polymer-based EL devices [12]. This is illustrated in the insert in Figure 2b which demonstrates a linear dependence of $\lg[J/U^2]$ on $1/U$. This corresponds to the Fowler-Nordheim law $J \sim U^2 \exp(-C/U)$ (C is a parameter depending on the shape of a potential barrier at the layer interface). Another confirmation of the tunnelling mechanism is the experimental fact that the change of a metallic cathode significantly vary the electric properties possibly due to changes of the metal work function [12].

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