Materials Science-Poland, Vol. 22, No. 4, 2004

New organic electroluminescent materials

M.G. KAPLUNOV[1*], S.S. KRASNIKOVA[1],
I.K. YAKUSHCHENKO[1], O.N. ERMAKOV[2], S.A. STAKHARNY[2]

[1]Institute of Problems of Chemical Physics, Russian Academy of Sciences,
142432, Chernogolovka, Moscow Region, Russia

[2]Joint-Stock Scientific and Technological Co "Sapfir", Moscow, Russia

Spectral and electric properties of six new materials for electroluminescent devices are described, including materials for emitting layers based on triazole derivatives and zinc chelate complexes, and a high-T_g hole -transporting material based on triphenylamine.

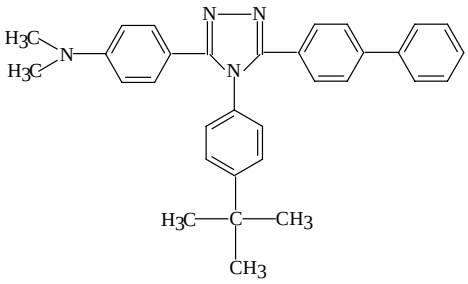
Key words: *organic electroluminescence; photoluminescence; new materials*

1. Introduction

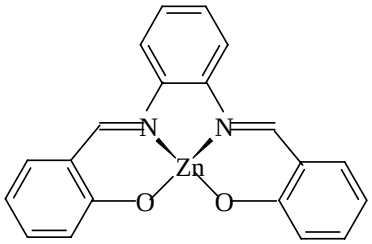
The study of organic electroluminescent (EL) materials is now a rapidly developing field of science due to promising practical applications [1, 2]. In spite of the impressing achievements of the last decade, the problem of searching for new effective luminescent materials of different emission colours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

In the present work, we report a study of spectral and electroluminescent properties for some new materials. The chemical structures of the materials studied are shown in Fig. 1.

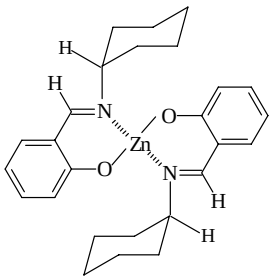
[*]Corresponding author, e-mail:kaplunov@icp.ac.ru.



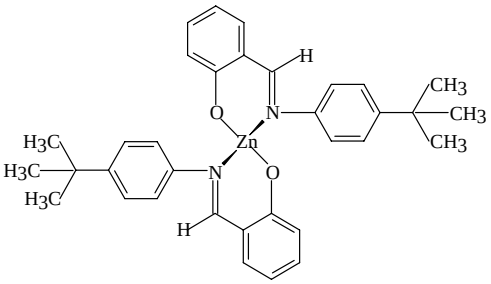
DA-BuTAZ



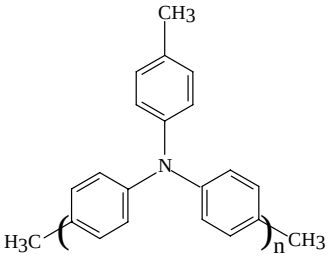
Zn(OB-PDA)



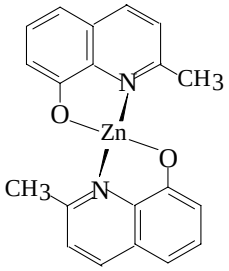
$Zn(OBCG)_2$



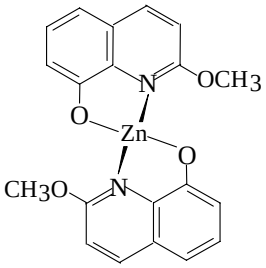
$Zn(OBBA)_2$



PTA



$Zn(CH_3Q)_2$



$Zn(MeQ)_2$

Fig. 1. Chemical structures of the materials studied

3-(4-dimethylaminophenyl)-4-(4′-*tert*-butylphenyl)-5-diphenyl-1,2,4-triazole or DA-Bu TAZ, is a promising 1,2,4-triazole derivative for blue emitting layer [3].

Zinc complexes containing the azomethine group –CH=N–R (R is an alkyl group) and characterized by blue electroluminescence have been recently proposed [4]. We have synthesized three new electroluminescent materials based on zinc chelate complexes with azomethine groups, which are characterized by electroluminescence in the blue and green spectral regions: bis(N-(2-oxybenzylidene)cyclohexylamine)-zinc, ($Zn(OBCG)_2$), N,N′-bis(2′-oxybenzylidene)-1,2-phenylenediamine-zinc, (Zn(OB-PDA)), and bis(N-2-oxybenzylidene)-4-*tert*-butylanyline)-zinc ($Zn(OBBA)_2$) [5]. The addition of various substituents at the nitrogen atoms or bridges between them enables changing the position of the absorption and luminescence spectral maxima due to changes in the electron density and conjugation length. Also, new Zn complexes with quinoline derivatives, bis(2-methoxy-8-oxyquinoline)zinc ($Zn(MeQ)_2$) and bis(2-methyl-8-oxyquinoline)zinc ($Zn(CH_3Q)_2$) were synthesized and studied.

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, or N,N′-diphenyl-N′N′-bis(3-metylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD), is a well-known hole-transporting material exhibiting excellent hole injection and transport capability with good electron-blocking capability at the HTL boundary. It is not very stable, however, due to its low T_g value [6]. Oligomers of triphenylamine with an oligomerisation number n in the range of 2–5 have been shown to have good hole-transporting characteristics, and the T_g for these materials is shown to increase with increasing n – from 60 °C for TPD to 140 °C for the oligomer with n = 5 [6]. PTA is a mixture of triphenylamine oligomers of a general formula shown above with oligomerisation numbers n from 7 to 11, characterized by the T_g as high as 185 °C [3].

2. Experimental

The synthesis of the materials 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 the spin casting of PTA or by the 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 recorded simultaneously with a computer-controlled potentiostat PI-50 and a calibrated photomultiplier, or with a Hewlett-Packard semiconductor parameter analyser HP4155A and Si photodiode. The technique for measuring the absorption and photoluminescence (PL) spectra and PL quantum yields is described elsewhere [7].

3. Results and discussion

Figure 2 shows the absorption and photoluminescence (PL) spectra for the evaporated films of the studied materials. For the zinc chelate complexes, the maximum with the longest wavelength absorption band shifts to longer wavelengths in the order: $Zn(OBCG)_2$, $Zn(OBBA)_2$, Zn(OBPDA). In the PL spectra, the broad bands (a half -width of about 100 nm) with maxima at 453, 510, and 565 nm, correspondingly, are observed shifting to longer wavelengths in the same sequence. For DA-BuTAZ films, the PL maximum is observed at about 430 nm. We have measured the PL quantum yield for DA-BuTAZ and PTA in benzene solutions, being estimated at about 90% and 70%, respectively. We have estimated the PL quantum yields of evaporated films of zinc complexes at 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, these quantum yields are comparable or higher than that of the well-known tris-8-oxiquinolate aluminium Alq_3, for which the PL quantum yield is reported to vary from 8–10 to 32% depending on the source of data [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 a maximum at 625 nm and a quantum yield of about 100%, which is due to electron excitation energy transfer from $Zn(OBBA)_2$ molecules to NR molecules [7, 9]. Spectral properties of the materials studied are summarized in Table 1.

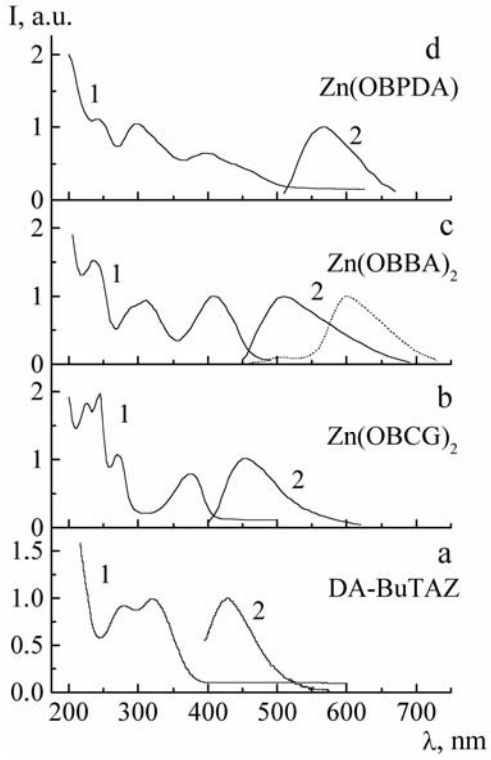


Fig. 2. Absorption (1) and photoluminescence (2) spectra of the materials: a) DA-BuTAZ, b) $Zn(OBCG)_2$, c) $Zn(OBBA)_2$ (dashed curve – PL of the film containing 0.5% of Nile Red), d) Zn(OBPDA)

Typical current–voltage and brightness–voltage characteristics of the studied devices with a ITO/TPD/DA-BuTAZ/Al structure are shown in Fig. 3a. Exchanging TPD with PTA does not principally change the electric and luminous properties, but systems with PTA are more stable at high currents. Exchanging the Al cathode with a 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 (down to 8–10 V for DA-BuTAZ). The EL properties of the materials with a ITO/PTA/EML/Mg:Ag structure are given in Table 1.

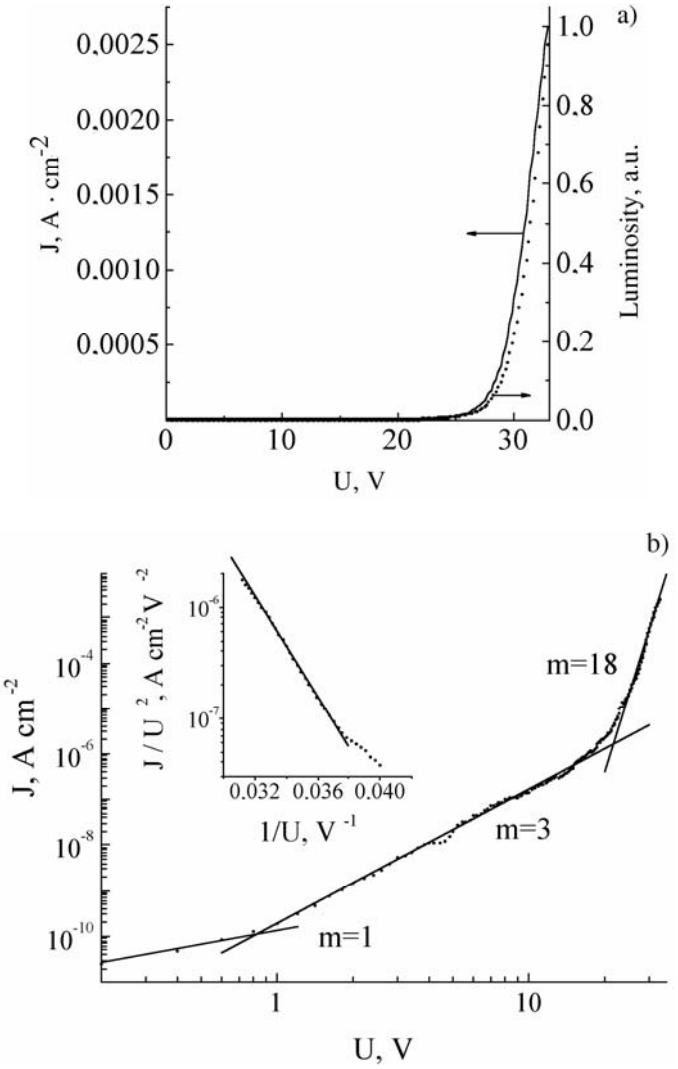


Fig. 3. Typical current–voltage and brightness–voltage characteristics of the EL device ITO/TPD/DA-BuTAZ/Al (a) and the current-voltage curve of the same device in a double logarithmic scale (b); the insert shows a part of this curve in the Fowler–Nordheim coordinates: J/U^2 vs. $1/U$

Table 1. Absorption, photoluminescence (PL), end electroluminescence (EL) of the materials studied

Compound	Colour	Absorption λ_{max}, nm	PL λ_{max} ($\Delta\lambda$) nm	PL QY, %	EL λ_{max} ($\Delta\lambda$) nm	Brightness, cd/m^2 (at voltage, V)	EL efficiency, cd/A
DA-BuTAZ	blue	320	430 (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
$Zn(CH_3Q)_2$	green	374	514 (100)	–	–	10 (50)	0.05
$Zn(MEQ)_2$	green	386	520 (100)	–	–	140 (14.8)	2.8
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	–	–	–

Figure 3b shows the dependence of the current density J on voltage U in the double logarithmic scale. Three regions can be seen in the current–voltage curve. At low voltages (less than 1 V), the current is proportional to voltage, which is the usual Ohmic behaviour. Beyond the Ohmic region up to the electroluminescence threshold, the dependence of the current on voltage follows a power law ($J \sim U^m$). Such a behaviour is characteristic of trap-controlled space charge-limited currents, and indeed it has been observed in EL devices based on Alq_3 and polymers with m changing from 2 to about 10 [10, 11]. The third region (beyond the light appearance threshold) may be characterized by a power low with a very high power index m (18–30), much higher than usually observed [10, 11]. An alternative explanation for this region is the injection limitation of current, for example by the Fowler–Nordheim tunnelling mechanism, which has been shown to be appropriate for some polymer based EL devises [12]. This is illustrated in the inset in Fig. 3b, which demonstrates a linear dependence of $\log(J/U^2)$ vs. $1/U$. This corresponds to the Fowler–Nordheim law: $J \sim U^2 \exp(-C/U)$ (C is a parameter depending on the shape of the potential barrier at the layer interface). Another confirmation of the tunnelling mechanism is the experimental fact that changing the metallic cathode significantly changes the electric properties, possibly due to changes in the metal work function [12].

Acknowledgement

This work was supported by the Russian Foundation for Basic Research, grant N 03-03-32199.

References

[1] MITSCHKE U., BAUERLE P., J. Mater. Chem., 10 (2000), 1471.
[2] BRAUN D., Materials Today, June 2002, 32.

[3] YAKUSHCHENKO I.K., KAPLUNOV M.G., EFIMOV O.N., BELOV M.YU., SHAMAEV S.N., Phys. Chem. Chem. Phys., 1 (1999), 1783.
[4] SANO T., NISHIO Y., HAMADA Y., TAKAHASHI H., UZUKI T., SHIBATA K., J. Mater. Chem., 10 (2000), 157.
[5] KAPLUNOV M.G., YAKUSHCHENKO I.K., KRASNIKOVA S.S., SHAMAEV S.N., PIVOVAROV A.P., EFIMOV O.N., Russ. Chem. Bull., in press.
[6] TANAKA H., TOKITO SH., TAGA Y., OKADA A., Chem. Commun. (1996) 2175.
[7] PIVOVAROV A.P., KAPLUNOV M.G., YAKUSHCHENKO I.K., BELOV M.YU., NIKOLAEVA G.V., EFIMOV O.N., Russ. Chem. Bull. 51 (2002) 67.
[8] GIRO G., COCCHI M., DI MARKO P., FATTORI V., DEMBECH P., RIZZOLI S., Synth. Met., 123 (2001), 529.
[9] PIVOVAROV A.P., KAPLUNOV M.G., EFIMOV O.N., YAKUSHCHENKO I.K., BELOV M.YU., Mol. Cryst. Liq. Cryst., 361 (2001), 263.
[10] IOANNIDIS A., FORSYTHE E., GAO Y., WU M.W., CONWELL E.M., Appl. Phys. Lett., 72 (1998), 3038.
[11] MARAI F., ROMDHANE S., HASSINE L., MAJDUB M., BOUCHRIHA H., Synth.Met., 132 (2003), 117.
[12] PARKER I.D., J. Appl. Phys., 75 (1994), 1656.

Received 14 October 2004
Revised 22 November 2004