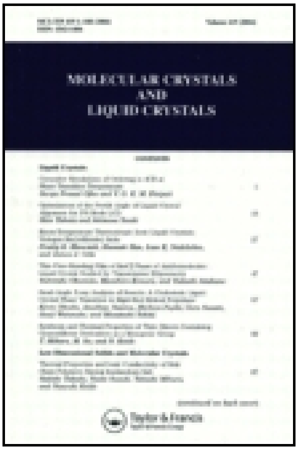

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New Organic Electroluminescent Materials Based on Chelate Metal Complexes

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New Organic Electroluminescent Materials Based on Chelate Metal Complexes

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We have synthesized some new chelate metal complexes based on 8-mercaptoquinoline and 8-aminoquinoline derivatives with different metals (Zn, Cd, Ga) and studied their spectral and electroluminescent properties. This is the first use of the compounds containing other heteroatoms instead of oxygen atoms in chelate cycles for OLED applications. The new compounds are characterized by blue and green luminescence. OLEDs prepared on the base of the new materials exhibit bright light emission with an efficiency of about 10 cd/A.

Keywords: aminoquinolines; mercaptoquinolines; organic electroluminescence

INTRODUCTION

The study of organic electroluminescent materials is now a rapidly developing field of science due to the promising practical applications in organic light-emitting diodes (OLED) [1,2]. In spite of the impressing achievements of the last decade, the problem of searching for the new materials as structures for organic electroluminescent devices is still topical.

Active electroluminescent materials should possess the efficient luminescence and good electron transport properties. Among these materials, chelate metal complexes play an important role [2]. An example is the well-known aluminum 8-hydroxyquinolate (Alq_3) [3], its zinc analog Znq_2 [4–6], and other compounds based on 8-hydroxyquinoline deriva-

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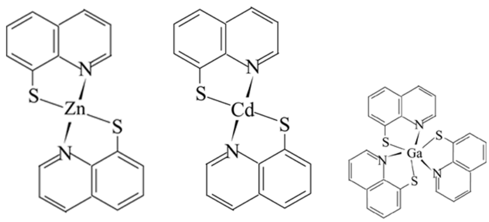
tives [7–10]. Other examples are zinc complexes with azomethine groups [5,11,12], complexes of benzothiazoles, and other heterocyclic ligands [5,6,13,14]. In all cases, chelate cycle contains a chain oxygen-metal-nitrogen. It is of interest to prepare the compounds containing other heteroatoms instead of oxygen atoms in chelate cycles for OLED applications.

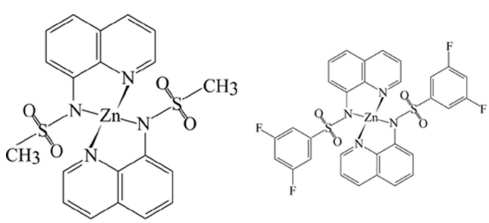
In the present work, we report some new metal complexes based on 8-mercaptoquinoline and 8-aminoquinoline derivatives with different metals (Zn, Cd, Ga) and studied their spectral and electroluminescent properties. The new compounds are characterized by blue-green and green luminescence. OLEDs prepared on the base of the new materials exhibit bright light emission with an effectiveness of up to 10 cd/A.

We have synthesized three new electroluminescent materials based on Zn, Cd, and Ga chelate complexes with 8-mercaptoquinoline. The chemical structures of the materials studied are as follows:



Zn(MQ)$_2$ Cd(MQ)$_2$ Ga(MQ)$_3$

We have also synthesized two new electroluminescent materials based on Zn chelate complexes with 8-aminoquinoline derivatives bis-[8-(methylsulfanylamino)quinolinate] zinc, Zn(M-SAMQ)$_2$ and bis-[8-(3,5-difluorophenylsulfanylamino)quinolinate] zinc, Zn(DFP-SAMQ)$_2$. The chemical structures of the materials studied are as follows:



Zn(M-SAMQ)$_2$ Zn(DFP-SAMQ)$_2$

EXPERIMENTAL

Synthesis

Ligands for aminoquinoline complexes were synthesized by the interaction of 8-aminoquinoline with corresponding sulfochloride

RSO_2Cl where R is CH_3 or $C_6H_3F_2$ and then transferred to Na salts by the interaction with Na methylate. Zn complexes were synthesized by the interaction of the Na salt of the corresponding ligand with $ZnCl_2$. Mercaptoquinolates of Zn, Cd, and Ga were synthesized by the interaction of the Na salt of 8-mercaptoquinoline with, correspondingly, $ZnCl_2$, $CdBr_2$ and $Ga(NO_3)_3$. Details of the synthesis will be described elsewhere [15].

Preparation of electroluminescence devices. Glass supports covered with transparent conducting indium—tin oxide In_2O_3—SnO_2 (ITO) were used as anodes with a resistance of $\sim 20\,\mathrm{Ohm \cdot cm^{-2}}$. A hole-transporting layer (a mixture of triphenylamine oligomers (PTA)) [16] was deposited on the anode by pouring from a solution

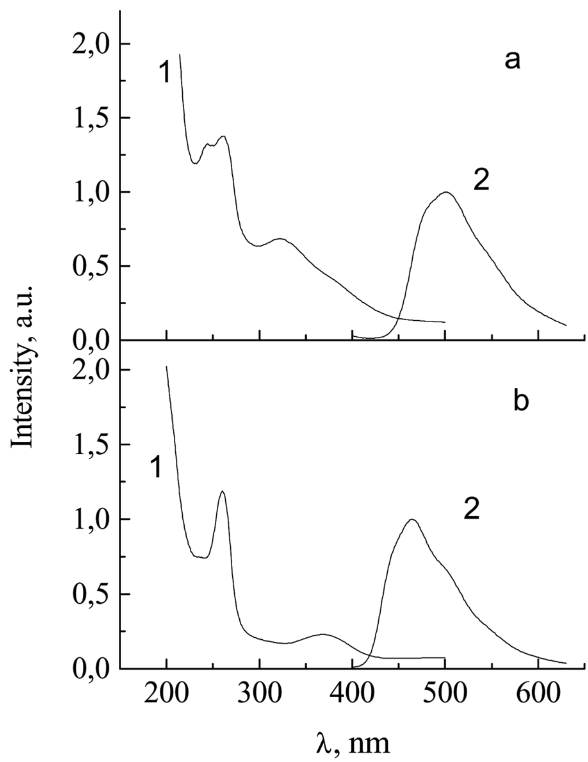


FIGURE 1 Absorption spectra of evaporated films (1) and fluorescence spectra of powders (2) for 8-aminiquinolinates: (a) bis-[8-(methylsulfanylamino)quinolinate] zinc, $Zn(M\text{-}SAMQ)_2$ and (b) bis-[8-(3,5-difluorophenylsulfanylamino)quinolinate] zinc, $Zn(DFP\text{-}SAMQ)_2$.

in toluene. 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 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 PI50 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 photomultiplier, taking into account the geometry of the setup and the passport sensitivity of a multiplier.

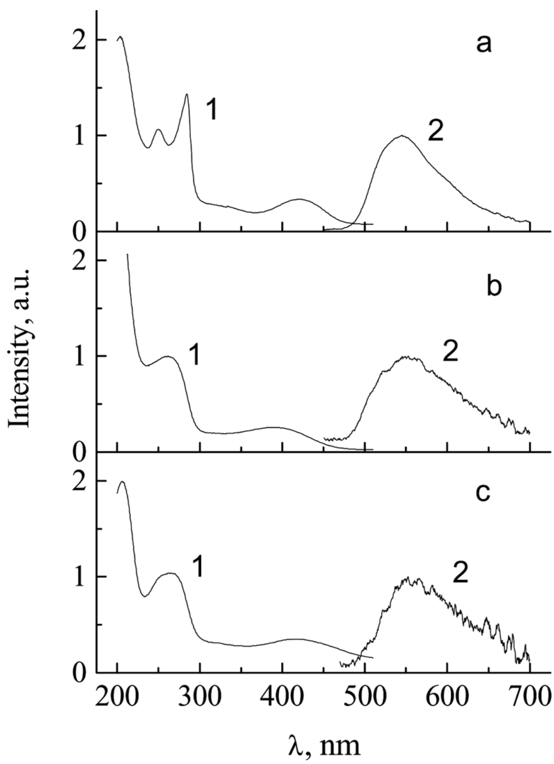


FIGURE 2 Absorption spectra of evaporated films (1) and fluorescence spectra of powders (2) of 8-mercaptoquinolinates: (a) $Zn(MQ)_2$, (b) $Cd(MQ)_2$ and (c) $Ga(MQ)_3$.

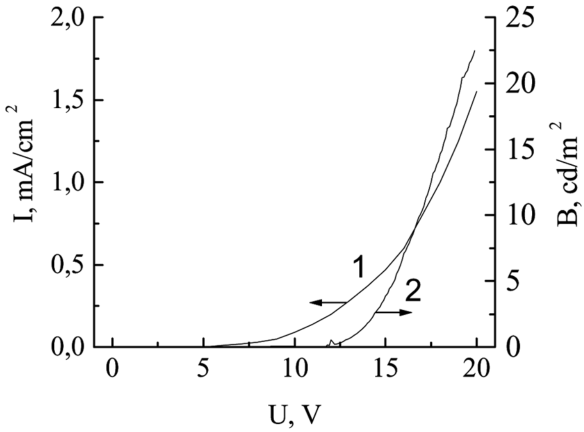


FIGURE 3 Current-voltage (1) and brightness-voltage (2) curves of ITO/PTA/Zn(M-SAMQ)$_2$/Al.

Spectral properties. Samples for measuring the absorption spectra were prepared by vacuum evaporation onto a quartz substrate. Photoluminescence spectra were measured for evaporated films and for powder samples. The absorption spectra were measured in the region of 200–900 nm with a Specord M40 spectrophotometer. The photoluminescence spectra were measured with an Ocean Optics

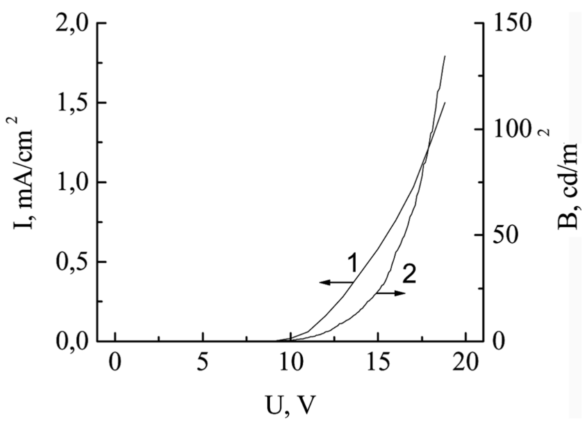


FIGURE 4 Current-voltage (1) and brightness-voltage (2) curves of ITO/PTA/Zn(DFP-SAMQ)$_2$/Al.

PC1000 plug-in spectrometer with the excitation from a light-emitting diode at 380 nm.

RESULTS AND DISCUSSION

Figures 1 and 2 show the absorption spectra of evaporated films and photoluminescence (PL) spectra of powders for the materials studied. $Zn(M\text{-}SAMQ)_2$ exhibits the absorption maxima at 245, 260, and 322 nm and a shoulder at 380 nm. $Zn(DFP\text{-}SAMQ)_2$ exhibits the absorption maxima at 260 and 368 nm. PL spectra of two complexes show bands with a half-width of about 100 nm and the maxima at 501 nm for $Zn(M\text{-}SAMQ)_2$ and 464 nm for $Zn(DFP\text{-}SAMQ)_2$.

The $Zn(MQ)_2$ spectra exhibit the maxima of absorption at 251, 285, and 421 nm and PL at 547 nm. $Cd(MQ)_2$ exhibits the absorption at 262 and 391 nm and PL at 550 nm. $Ga(MQ)_3$ exhibit the absorption at 265 and 416 nm and PL at 580 nm. Cd and Ga complexes show a much less effective PL comparing to that of the Zn complex.

We have prepared the electrolumimescent devices based on $Zn(M\text{-}SAMQ)_2$, $Zn(DFP\text{-}SAMQ)_2$, and $Zn(MQ)_2$. The typical current-voltage and brightness–voltage curves are shown in Figures 3–5. The device with $Zn(DFP\text{-}SAMQ)_2$ shows the brightness by about 6 times higher than that of $Zn(M\text{-}SAMQ)_2$ and gives the efficiency of about 10 cd/A even with an Al cathode. This is a rather good result comparing with 1–4 cd/A which is typical of oxygen-containing metal chelate

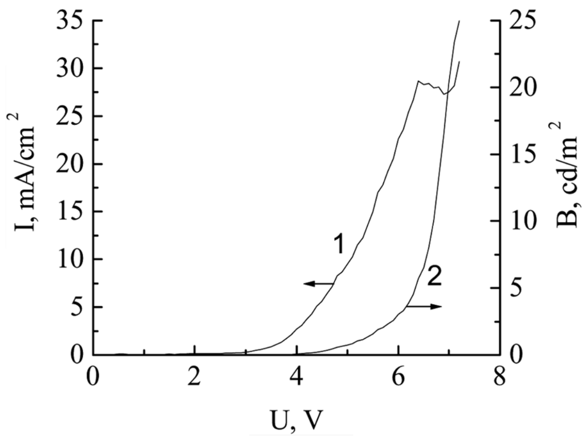


FIGURE 5 Current-voltage (1) and brightness-voltage (2) curves of ITO/PTA/$Zn(MQ)_2$/Mg:Ag.

complexes [5–8]. The device based on $Zn(MQ)_2$ showed rather bad results comparing with that for aminoquinoline complexes.

CONCLUSION

We have synthesized some new metal complexes based on 8-mercapto-quinoline and 8-aminoquinoline and prepared OLEDs on the base of the new materials. To our knowledge, this is the first use of chelate metal complexes containing other heteroatoms instead of oxygen atoms in chelate cycles for OLED applications. OLEDs based on 8-aminoquinoline exhibit the bright light emission with a good efficiency of about 10 cd/A, which shows that the new type of chelate metal complexes may be of interest for the use in OLEDs.

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