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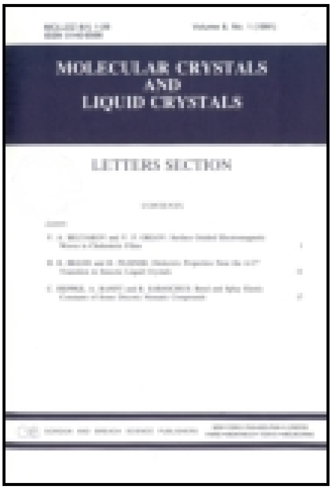

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Some Metal Complexes of 9-Hydroxyphenalenone as Novel Electron Transporting Materials for OLEDs

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Some Metal Complexes of 9-Hydroxyphenalenone as Novel Electron Transporting Materials for OLEDs

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Aluminum, zinc, beryllium and lithium complexes with 9-hydroxyhyphenalenone are synthesized, and their spectral properties for powders and films are measured. These complexes may be appropriate of applying them for OLEDs. An example of electroluminescent device based on the beryllium complex is presented.

Keywords 9-hydroxyhyphenalenone; metal complexes; OLEDs

Introduction

The complexes of some metals (aluminum, zinc, beryllium etc.) with 8-hydroxyquinoline (e.g. AlQ_3) and (or) 2(2-hydroxyphenyl)benzothiazole are widely used as electron transporting materials in organic light emitting diodes (OLEDs) due to their high photoluminescence in solid state and high electron mobility [1–3]. However, these materials have some disadvantages for practical use. They oxidized and hydrolyzed readily by traces of oxygen and water in real devices. Besides, the crystallization if initially amorphous material can take place during exploitation of the device [4–7]. Thus search of new metal complexes deprived of such disadvantages is of importance. An appropriate example of such complexes could be metal complexes of 9-hydroxyphenalenone. Al complex of this ligand was noted as chemically and thermally stable material [8,9]. It was pointed out that the electrophysical properties of aluminum complex with 9-hydroxyphenalenone as an electron-transporting material are comparable with that of AlQ_3 but the thermal stability of this complex is much higher than that of AlQ_3 [8]. Some metal complexes of 9-hydroxyphenalenone were described in literature [8,10–15]. However very few works are devoted to application of 9-hydroxyphenalenone metal complexes to OLEDs [8,13]. All this is evidence in favor of necessity of more comprehensive study of 9-hydroxyphenalenone metal complexes as the electron-transporting materials for OLEDs.

The aim of our work is the investigation of some metal complexes of 9-hydroxyphenalenone as materials for OLEDs. We synthesized aluminum, zinc, beryllium and lithium complexes with 9-hydroxyhyphenalenone and measured their spectral properties for powders and films. The electroluminescent device based on beryllium complex was prepared.

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Experimental

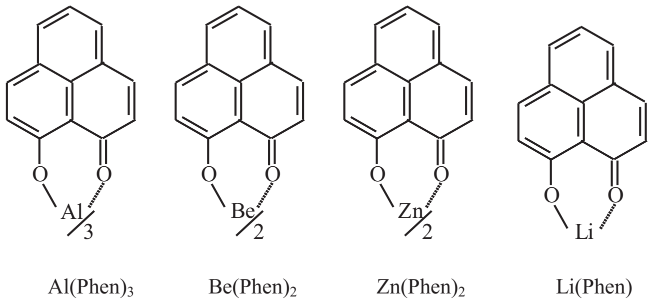
9-hydroxyphenalenone was synthesized as described in references [9,16,17]. Complexes of Al, Zn and Be were synthesized according to our method. First, suspension of 9-hydroxyphenalenone in methanol was treated with the equimolar amount of sodium methylate with the formation of sodium salt of 9-hydroxyphenalenone. Then the stoichiometric amount of corresponding metal salt dissolved in methanol or water was added to the sodium salt. Li complex was synthesized by interaction of the suspension of 9-hydroxyphenalenone in methanol with the equimolar amount of lithium methylate. Metal complexes were then recrystallized from corresponding solvents. In the IR spectra of metal complexes, the absorption bands are observed in the region of 1629, 1580–1585, 1512–1527, 1255–1275 and 1243 cm^{-1} which is close to that of reported for 9-hydroxyphenalenone and its Al, Be, Zn complexes [9–11,17]. Molecular structures of Al, Be, Zn complexes are described in literature [8,11]. In particular, for $Be(Phen)_2$ the coordination around beryllium atom is pseudo-tetrahedral with the two almost plane Phen ligands being near perpendicular to one another [11].

The infrared spectra were measured on Perkin-Elmer Spectrum-100 FT-IR spectrometer for powders by the attenuated total reflectance method on Ge prism. The UV-VIS absorption spectra were measured on the Specord M40 UV-VIS spectrophotometer in the region of 200–900 nm. Samples were the films deposited from toluene solution or the powders rubbed on a quartz plate. The photoluminescence and the electroluminescence spectra were measured on the Ocean Optics QE65000 fiber optics spectrometer in the region of 450–900 nm. Samples for the photoluminescence were powders and films deposited from toluene solution; a 380 nm light-emitting diode was used for excitation.

The electroluminescent device was prepared on glass substrate coated with indium-tin oxide (ITO) transparent anode. First the hole-injecting layer of PEDOT:PSS [18] was spin-coated on ITO layer. Then the emitting layer was spin-coated on PEDOT:PSS layer from the blended organic solution. The solution consisted of the host material poly(N-vinylcarbazole) (PVK), the hole-transporting material oligomer of triphenylamine (PTA) [19] and the electron-transporting and emitting material - the metal complex of 9-hydroxyphenalenone. Finally the Al:Ca alloy was vacuum evaporated on the emitting layer as an anode.

Results and Discussion

We have synthesized and studied spectral properties of four metal complexes of 9-hydroxyphenalenone with aluminum $Al(Phen)_3$, beryllium $Be(Phen)_2$, zinc $Zn(Phen)_2$ and lithium Li(Phen) (Scheme 1).



Scheme 1. Molecular structures of studied metal complexes [8,11].

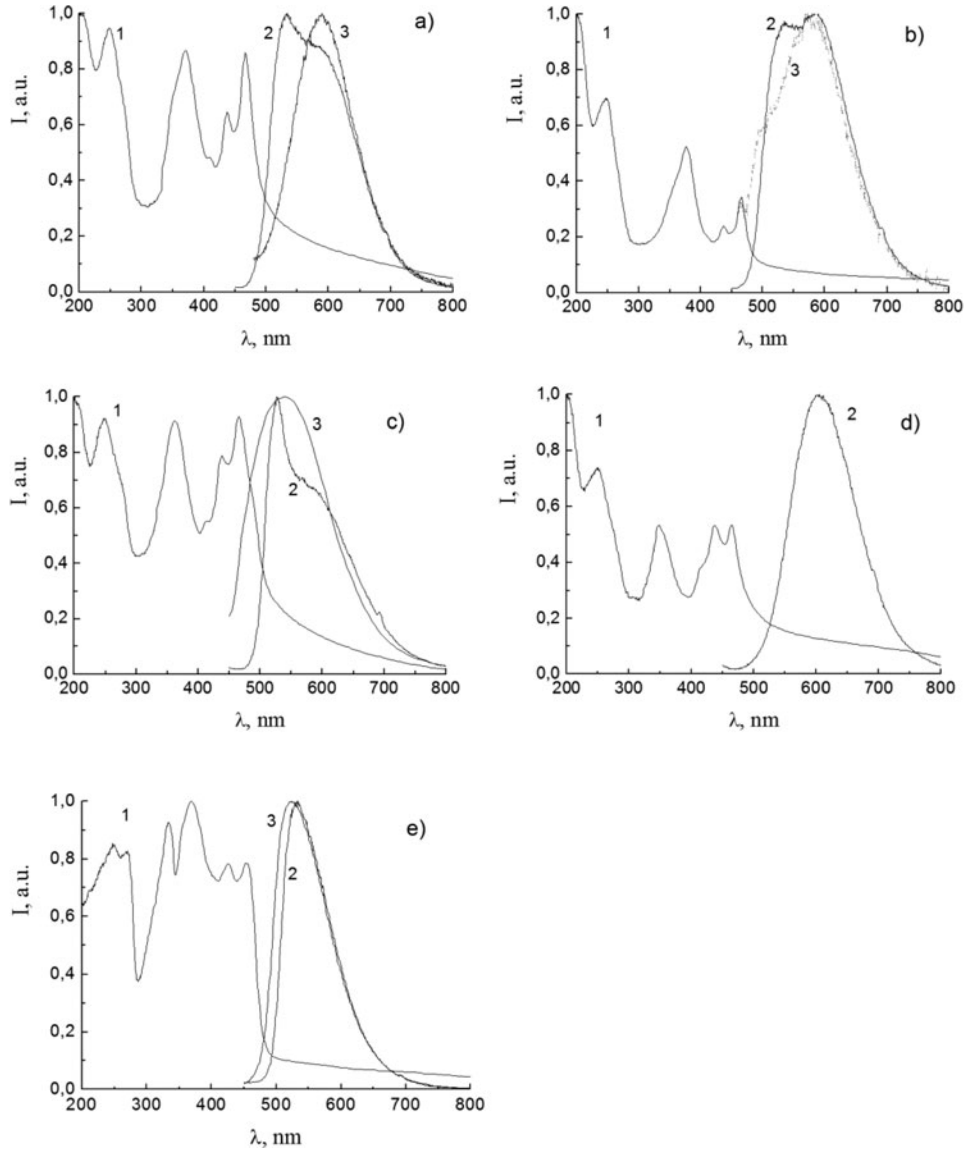


Figure 1. Absorbance spectra (1) and photoluminescence spectra of powders (2) and films (3) of Al(Phen)$_3$ (a), Be(Phen)$_2$ (b), Zn(Phen)$_2$ (c), Li(Phen) (d) and 9-hydroxyphenalenone (e).

Figure 1 shows the absorption and photoluminescence spectra of Al(Phen)$_3$, Be(Phen)$_2$, Zn(Phen)$_2$ and Li(Phen) complexes as well as 9-hydroxyphenalenone ligand. The absorption spectra of all the complexes are similar and exhibit intensive peaks at about 200, 250, 360, 440 and 465 nm. The absorption spectra of the complexes resemble that of 9-hydroxyphenalenone ligand with the exception that the band about 200 nm is absent in the spectrum of ligand and the band 335 nm is present in the spectrum of ligand but is absent in the spectra of complexes. Besides, the most long-wavelength band 455 nm in the spectrum of ligand is shifted to 456 nm in the spectra of complexes.

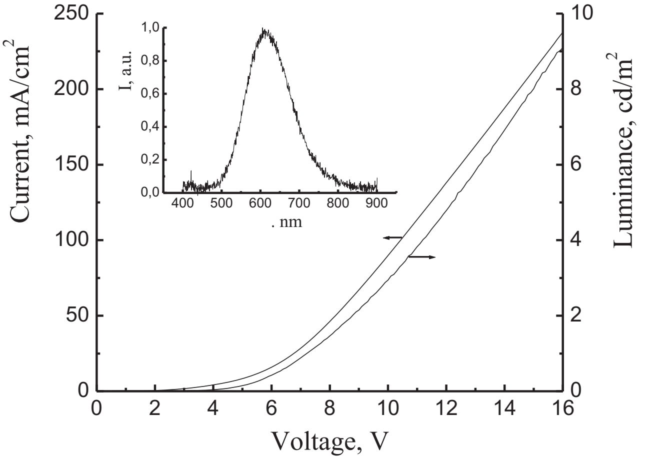


Figure 2. Typical current-voltage and luminance-voltage characteristics for the ITO/PEDOT:PSS/PVK:Be(Phen)$_2$:PTA/Al:Ca device. The insert shows the electroluminescence spectrum of this device.

Figure 1 also shows the photoluminescence spectra of 9-hydroxyphenalenone ligand and its metal complexes. The photoluminescence spectra are shown for the powders (curves 2) and the films deposited on glass plates from toluene solutions. For Li(Phen) complex, only powder spectrum was measured due to low solubility of this complex. The powder photoluminescence spectra of Al, Be and Zn complexes exhibit wide band in the yellow-orange region about 500–650 nm with two maxima at about 530 and 590 nm with the whole half-width about 150 nm. The film spectra of these complexes exhibit single bands with maxima at about 600 nm and half-widths of about 120 nm. For Al(Phen)$_3$, the photoluminescence spectrum of the film is similar to that reported for the evaporated film of this complex [8]. The spectrum of Li complex exhibits single PL band with maximum at about 600 nm and half-width of about 100 nm. The spectrum of 9-hydroxyphenalenone ligand exhibits single PL band both for powder and film samples with maximum at about 530 nm and half-width of about 100 nm.

We have roughly estimated quantum yields of photoluminescence for powders of 9-hydroxyphenalenone and its Al, Be, Zn, Li complexes by method described elsewhere [20]. In all cases quantum yields are not high and lie in the region of 3–4%. So these materials can be employed in electroluminescent devices as emitting (but not very effective) components and as electron-transporting materials with more effective emitters.

As an example of employing the 9-hydroxyphenalenone metal complexes in OLEDs, the electroluminescent device based on beryllium complex Be(Phen)$_2$ was prepared. The luminescent layer was deposited by spin coating from toluene solution containing PVK, Be(Phen)$_2$ and PTA in proportion 8:1:1. Figure 2 shows typical current-voltage and luminance-voltage characteristics for the ITO/PEDOT:PSS/PVK:Be(Phen)$_2$:PTA/Al:Ca device. The threshold of light appearance is about 4 V which is essentially less than that of similar device based on Nd(Phen)$_3$ complex (about 25 V) [13]. Current and luminance values for our device are similar to that of Nd(Phen)$_3$ based device [13]. The insert in figure 2 shows the electroluminescence spectrum of this device. The band with maximum at about 620 nm and half-width of about 130 nm which is similar to that of photoluminescence band of Be(Phen)$_2$ film (figure 1b). The electroluminescence of the device is obviously due to Be(Phen)$_2$ complex since PVK and PTA are characterized by blue luminescence (about 420–450 nm) [13,19].

Conclusion

Spectral properties of some 9-hydroxyphenalenone metal complexes were investigated. These complexes cam be used as electron-transporting and emitting materials in electroluminescent devices.

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