Ultraviolet electroluminescence from organic light-emitting diode with cerium(III)--crown ether complex

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Received 22 August 2006; received in revised form 24 April 2007; accepted 8 May 2007

The review of this paper was arranged by Prof. Y. Arakawa

Abstract

Cerium-dicyclohexano-18-crown-6 complex, Ce-DC-18ÆCÆ6, was prepared and used to fabricate organic light-emitting diode (OLEDs) with structure of ITO (indium tin oxide)/CuPc (copper-phthalocyanine)/Ce-DC-18ÆCÆ6: CBP (4,4'-bis(9-carbazolyl)biphenyl)/Bu-PBD (2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole)/LiF/Al. In the device the emitter layer consists of Ce(III)-complex as a dopant and CBP as a host. Adopting this doping Ce(III)-complex film, the device exhibits ultraviolet (UV) emission at 376 nm and maximum UV radiance power 13 lW/cm² at 3 wt% Ce(III)-complex doped device is obtained, which has been improved by about two times in comparison with no Ce(III)-complex layer UV device. In terms of photoluminescence (PL) of Ce(III) ion and CBP film, we demonstrated that the two UV emissions should be assigned to be from electron transitions of 5d ! 4f of the Ce(III) ion and of S1 ! S0 of CBP molecule, respectively. Increasing in UV radiation at shorter UV wavelength is more valuable and interesting for solid lighting application because the shorter UV emission would much match with excitation bands of more organic or inorganic phosphors. The mechanism on the electroluminescence (EL) processes of Ce(III) ion was also discussed.

Keywords: Ultraviolet-OLED; Ce(III)-complex; 5d ! 4f transition; UV radiation source

1. Introduction

Since the report of efficient electroluminescence (EL) from a bilayer organic light-emitting diode (OLED) by Tang and VanSlyke [1], EL diodes based on organic materials have attracted considerable interest and constitute a rapidly developing field due to their potential use in the development of energy-efficient, low-cost, full-color, flat-panel displays and other emissive products [2–11]. Light-emitting materials for OLED can sketchily be classified into three types according to their molecular structure: organic dyes [6], metal complexes [1], and polymers [12].

Motivated by the success of tris(8-hydroxyquinoline) aluminum (Alq3) in vacuum-deposited OLEDs, metal-complexes have particularly attracted a lot of attentions. Metal complexes offer many attractive properties, such as displaying a double role of electron transport and light emission, higher thermal stability, and easy of sublimation. Moreover, an attractive feature of these complexes have the ability to generate a much greater diversity of tunable properties and their emission color by virtue of the coordinated metal center or by modifying the backbone substituents of ligands. In the chelate metal complexes, the trivalent lanthanide-based materials have become promising phosphors for EL devices. Because these complexes generally exhibit extremely sharp, well defined spectral lines because the emission originated from the lanthanide...
(Ln(III) ions which are dominated by parity forbidden f–f transitions, and those organolanthanide phosphors also offer the potential for high internal quantum efficiency up to 100%. Based on the advantages of lanthanide(III) complexes, several groups of workers, including ourselves [13–18], have extensively investigated and found many excellent OEL devices based Ln (III)-complexes. The emission of the Ln(III), however, indicated mainly visible EL emissions with f–f transitions [13–20], and shows phosphorescent decay time, such as lifetime of the excited time is millisecond level due to their forbidden electron transition [21]. But there is a very shorter the excited state lifetime (10^{-7}–10^{-8}s) of Ce3+ ion in inorganic system [22] and in its complex [23] due to parity-allow 5d → 4f transitions of the Ce(III) ion [22]. Such a short decay time would have benefit because it can match with that of organic fluorescent EL. Besides, broad emission spectrum of Ce(III) ion is in favor of excitation of the phosphors for solid state lighting because excitation bands of more phosphors have wide band feature. There is, however, only one report on EL based the allowed 5d → 4f transition of lanthanide complexes, which resulted from divalent europium (Eu2+) [24]. In the devices with Eu2+-complex, the EL did not only resulted from 5d → 4f transition, but also from a charge transfer transition, and the emission color indicated orange color with lower efficiency. On the other hand, UV radiation from solid state source has significance in illumination applications, because lot of phosphors can be excited by UV light at 250–380 nm. Thus, panel lighting source could carry out by combining red, green and blue phosphors. Furthermore, if inorganic phosphor was used as white light-emitting materials, only use the UV radiation source, the illumination would exhibit more high durability than single organic white EL. Moreover, the selection of UV-exciting phosphors would also become more flexible [25] than that of single blue light exciting inorganic LED [26]. Thus UV emitting OLEDs are gradually focused by some researchers [27–30]. However, UV emission of those UV OLEDs covered blue visible emissions, such as, UV emission from CBP-device reported by Shinar and Co-workers [30] the radioactive peak was at ~390 nm with shoulder bands at blue region, which will be poor for selecting phosphors because the excitation band is seldom at visible region. The Ce(III)-complex with crown ether can generally show strong UV photoluminescent emission resulted from the 5d → 4f transition [31,32], so device with Ce(III)-complex should give out an UV EL radiation and would be a UV EL exciting source for white solid state lighting.

In the present study, we used the Ce(III)–crown ether complex as an emitter to fabricate UV-device. The device with structure of ITO/CuPc (20 nm)/Ce-DC-18-C6: CBP (3 wt%, 75 nm)/Bu-PBD (65 nm)/LiF (1 nm)/Al (100 nm) was constructed, in which the CBP and the Ce(III)-complex were used as the host and the dopant of the UV emitter, respectively, although CBP contained UV device has been reported [30]. Comparing the EL and the PL spectra of the Ce(III)-complex and the CBP, whole UV EL radiation of the device can be demonstrated to be composed of the UV emission at shorter wavelength from Ce(III) ion and a part of longer UV emission from the CBP host.

2. Experimental

Anhydrous CeCl3 was prepared from CeCl3·6H2O (99.99%) which was dried at 100 °C for 4 h in a vacuum-constant temperature at 100 °C drying oven. Dicyclohexano-18-crown-6 was a Fluka chemical. 4,4′-Bis(9-carbazolyl) biphenyl (CBP) was purchased from Electro-Light Technology Corp. (Beijing) and purified by the train sublimation method for three times. Absolute methanol and chloroform were all analytical grade ones and purified for need.

2.1. Synthesis of Ce(III)–crown ether Complex

Dicyclohexano-18-crown-6 (1 g, 2.68 mmol) and chloroform (5 mL) were placed in a three-necked flask (50 mL), and then stirred at room temperature until the solid sample was dissolved completely. Then an absolute methanol solution (20 mL) of anhydrous CeCl3 (0.662 g, 2.68 mmol) was added dropwise into the reaction flask. In a dry nitrogen atmosphere, the mixture was stirred and refluxed at 60 °C for 10 h. After removing a majority of solvent under reduced pressure, a white precipitate was formed from the residue solution. The precipitate was re-crystallized from its methanol solution to give a white polycrystalline powder (1.4 g, 84%). Anal. Calc. for C_{32}H_{36}O_{6}Cl_{3}Ce (%): C, 38.81; H, 5.86. Found: C, 39.16; H, 5.43.

2.2. EL Device Fabrication

ITO-coated glass with a sheet resistance $R_{s} \sim 15 \Omega / \square$ was cut into 3 cm × 3 cm plates and etched in dilute hydrochloric acid for 20 min. Then it was ultrasonically cleaned for 10 min in detergent, deionized water, acetone and methanol. Finally, it was dried in a stream of dry nitrogen. The organic layers were sequentially deposited at a rate of 0.1–0.4 nm/s by thermal evaporation in a vacuum chamber (2 × 10^{-4} Pa). The emission area of the EL devices was 3 × 4 mm². A quartz crystal oscillator placed near the substrate was used to monitor the thickness of the thin films. The PL spectra of the Ce(III)-complex and the CBP films on surface of quartz substrates were determined.

2.3. Measurements of the PL and EL spectra

The PL and EL spectra of the samples were recorded with a Hitachi F-4000 Fluorescence Spectrophotometer, and the slits of emission and excitation were 5 nm. The irradiance of the light emission from the devices was measured with a UV irradiance meter, model UV-A (made in the Beijing Normal University, China), which consists of two ultraviolet detectors (UV-365 and UV-420) and a
readout unit connected to the probe by a cable. During measurement, we used the detector to probe UV irradiance power, which was corrected for the equipment sensitivity.

3. Results and discussion

The chemical structures of CuPc, CBP, Ce(III)-complex, Bu-PBD, and the OLEDs are shown in Fig. 1. CBP was used as the host material due to its good hole-transport properties, although NPB (N,N'-diphenyl-N,N'-bis(1-naphenyl)-1,1'-biphenyl-4,4'-diamine) was also commonly used as hole-transport material, it cannot be used in the UV devices due to its stronger blue emission.

Differing from the emission of other trivalent lanthanide complexes, the PL emission of Ce(III)-complex originates from a transition of allowed 5d→4f, and the emission peaks of Ce(III)-complex usually covered the UV region [23,31,32]. Although Ce 3+-activated inorganic phosphors were widely reported, the reports on the organic EL emission of Ce(III)-complex has not yet been published. Li et al. [31,32] have investigated the PL of Ce(III)-complex with 18-crown-6(18ÆCÆ6) and Ce(III)-18ÆCÆ6 complexes in polymer films, and have found that the Ce(III)-polymer complex emits strong UV fluorescence. Because the radius (1.2 Å) of the Ce(III) ion is comparable with the radius of cavity size (1.3 Å) of an 18-C-6 ring, complex of Ce(III) ion with 18-C-6 by a 1:1 molar ratio was easily formed, i.e. Ce(III) entered in the cavity of the crown ether.

In the present studies, we used dicyclopentano-18-crown-6 (DC-18-C-6) ether as the ligand of Ce(III) ion to synthesize Ce(III)-DC-18-C-6 complex, and the Ce(III)-DC-18-C-6 complex will potentially be expected to use emitting dopant material of UV EL diodes. Because there are two cyclohexane rings in the DC-18-C-6 molecule, the lipophilicity of the DC-18-C-6 should be greater than that of 18-C-6, but the two cyclohexane could not change the cavity size of the crown ether, moreover thin film EL device can easily be fabricated by thermally evaporating the Ce(III) complex in vacuum. In order to investigate the effect of the ligand on the fluorescence of the Ce 3+ in Ce(III)-DC-18-C-6 complex, excitation and fluorescence spectra of the Ce(III)-DC-18-C-6 complex and anhydrous CeCl 3 in methanol solution, as shown in Fig. 2, we can see that in the Ce-complex system there are two excitation bands centered, respectively, at ~255 and at ~313 nm and a broad emission band at ~360 nm. The two excitation bands are assigned to electron transition from ground state of 4f level to the splitting 5d level by coordination field, and the emission band is from the lowest splitting 5d level to the ground state (4f), which were the same as the results reported in Ref. [32]. For understanding the

![Fig. 1. Chemical structures of the materials used and the device structure.](image-url)
coordination of Ce(III) with DC-18-C-6, the excitation and emission properties of anhydrous CeCl₃ in methanol solution were observed (see Fig. 2) and it was noticed that the excitation bands peaked, respectively, at 283 nm and at 334 nm as well as a broad emission band at 376 nm were determined, showing that shifting to shorter wavelength of the excitation and emission of Ce(III)-DC-18-C-6 complex proved the coordination. And the two distinguishing excitation bands for the different systems were explained to be due to changed coordination environment surround the Ce(III) ion. In addition, the emission intensity of the Ce(III) in Ce(III)-DC-18-C-6 complex is considerably stronger than that of Ce(III) in anhydrous CeCl₃ at the same concentration in MeOH solutions, which again definitely proved that complex of the Ce(III) ion with the crown ether was formed.

Fig. 3 shows the PL spectra of the Ce(III)-DC-18-C-6 complex in methanol solution and in film deposited on a quartz substrate in vacuum. Thus, it is further illuminated that the complex film was easily deposited by vacuum evaporation. We can see that PL emissions from the film and its solution have the same spectrum feature although there is smaller difference at shorter wavelength, the PL should be attributed to above-mentioned electron transition from 5d to 4f [31,32].

To understand the dependence of UV emission of Ce(III)-complex on the CBP UV emission, changing of Ce(III)-complex concentration in the CBP host was studied, and it is noticed that for the strongest UV emission the optimum concentration is at 3 wt% Ce(III)-complex. When the concentration was lower 3 wt%, UV radiation from CBP would be dominated. But when it is higher than 3 wt%, the EL device does almost not work at high driving voltage, showing that the Ce(III)-complex exhibits poor carrier transporting property due to its non-conjugated feature. That is, CBP host material was doped by more Ce(III)-complex its hole-transport ability was considerably decreased so that its conductive property was intensively reduced.
The energy level diagram of CBP based EL device and CBP: Ce(III)-complex based EL device, respectively, are shown in Fig. 6(a) and (b). The singlet ($S_1$) and the triplet ($T_1$) excitons are synchronously formed when applying the forward bias to the device without Ce(III)-complex, and the UV emission occurs by $S_1 \rightarrow S_0$ electron transition of CBP emitter as shown in Fig. 6(a). For the device with the Ce(III)-complex as shown in Fig. 6(b), the UV EL emissions not only result from the CBP but also from the Ce(III)-complex. Under electrical excitation, the emission of CBP itself UV emission from the Ce(III) ion also occurs which RE ion displays 5d–4f allow transition is interesting project because wide UV emission band could occur.

**References**


Fig. 4 shows PL spectra of films of the Ce(III)-DC-18·C·6 complex and CBP, as well as EL spectra of device with (3 wt%) Ce-complex (device-A) and only CBP-host containing device (device-B), respectively. From Fig. 4 it is clearly shown that UV emission at shorter wavelength of the device A corresponds to PL emission of Ce(III)-complex film, and the UV EL peak was shifted to shorter wavelength comparing EL spectrum (at ~382 nm) of single CBP-device (device-B) and EL spectrum of the UV-diode reported in Ref. [30], although there is a shoulder at 395 nm. The result indicates that the origin of the short-wavelength band of the EL would be attributed to Ce(III) ion emission of the Ce(III)-complex because there could be not chromophore at near UV region of the DC-18-C-6 ligand with adipose structure. In UV emission of the Ce(III)-DC-18-C-6 complex doped CBP host, besides emission from the Ce$^{3+}$ ion, the emission from CBP host could also contribute the whole UV emissions.

The radiance–voltage ($R$–$V$) characteristics for the device A and B are shown in Fig. 5. The tun-on voltage is at about 9 V and 11 V for the device A and the device B, respectively, and the radiance of the device A is larger than that of the device B. The radiance of the devices increases with the increasing current density. The maximum radiances were reached up to 13.0 μW/cm² (at 22 V) and 7.3 μW/cm² (at 20 V) for the device A and B, respectively, indicating that the UV radiance of the device A is nearly two times than that of the device B. This result demonstrated that the Ce(III)-DC-18-C-6 complex could play an important role for increasing whole UV EL emission.

4. Conclusions

We reported on a UV emission OLED with the EL layer composed of the doped Ce(III)-DC-18-C-6 complex and the CBP host. The EL device with the structure of ITO/CuPc/Ce(III)-DC-18-C-6 complex: CBP/Bu-PBD/LiF/Al was employed to study the EL properties. UV EL emission at ~376 nm from Ce(III) ion was firstly observed. At the ratio of the Ce(III)-DC-18-C-6 complex to the CBP was 3 wt%, a maximum radiance of 13 μW/cm² was achieved at bias of 22 V. Our UV diode showed that UV EL emission with shorter wavelength could have better advantage than the device without Ce(III)-DC-18-C-6 complex reported in Ref. [30] in favor of applying for excitation source of inorganic phosphors because excitation spectra of most of phosphors lie shorter UV wavelength. Thus, the selecting field of the phosphors could be extended for facilitating design of solid state lighting source by combining the panel UV OLED with phosphors. It is demonstrated that developing EL device containing rare earth (RE) complex in which RE ion displays 5d–4f allow transition is interesting project because wide UV emission band could occur.

Acknowledgment

This work is supported by the National Science Significant Research Project of China (No. 90201012).