Electroluminescence of Bis[*N*-hexadecyl-8-hydroxy-2-quinoline carboxamide]cadmium

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An electroluminescent (EL) device with a single layer structure (ITO/emitting layer/Al) was constructed using an intensely fluorescent amphiphilic complex, bis[N-hexadecyl-8-hydroxy-2-quinoline carboxamide]cadmium ($Cd(HQ)_2$), for the emitter material. Greenish-yellow EL emission with a luminance of about 1200 cd/m^2 was observed with a low voltage drive (7 V).

In the last decade, the studies of electroluminescence (EL) in organic materials have concentrated on the thin-film-type devices made of Langmuir-Blodgett (LB) films,[1] vacuum-deposited films[2-7] or polymer films.[8,9] Tang et al.[2,3] reported firstly a two-layer-type organic EL device and found that an 8-hydroxy quinoline aluminum (Alq_3) complex can be used as an emitting element. In the EL diode they designed, high external quantum efficiency, luminous efficiency and brightness are achievable at a driving voltage below 10 V. After Tang's research works, other 8-hydroxyquinoline derivatives-metal complexes (such as Znq_2, Beq_2, Mgq_2, $Zn(mq)_2$, $Be(mq)_2$, $Al(prq)_3$) were also used as emitters.[4] Since 8-hydroxyquinoline chelates have unusual optical, electrical, magnetic, thermal and other physical properties, it is possible to prepare organic functional ultrathin films with a controlled thickness of a molecular size and with well-defined molecular orientation by LB film technique.[10,11] Evidently, if some new amphiphilic 8-hydroxyquinoline derivatives can be synthesized, they may be incorporated in LB films and have some potential application in EL devices.[12]

The synthesis procedure for an amphiphilic ligand, N-hexadecyl-8-hydroxy-2-quinoline carboxamide, HHQ, was prepared by the method described early[13] and the surface pressure-area isotherms of HHQ monolayers at the air-water interface on subphases containing metal ions were investigated.[14,15] A complex, bis[N-hexadecyl-8-hydroxy-2-quinoline carboxamide] cadmium, $Cd(HQ)_2$, was prepared by coordinating $CdCl_2 \cdot 2.5H_2O$ with HHQ in a boiling methanol solution. After washed with hot methanol several times, the complex $Cd(HQ)_2$ gave satisfactory analytical values. Anal. Calcd. for $C_{52}H_{78}N_4O_4Cd$: C, 66.81; H, 8.35; N, 6.00%. Found: C, 66.70; H, 8.00; N, 6.20%. The content of cadmium was titrated by EDTA after $Cd(HQ)_2$ was dissolved with 1:1 HNO_3-$HClO_4$. Calcd: 11.99%. Found: 11.79%.

The EL devices had a single layer of organic material sandwiched between two injecting electrodes: ITO / emitting layer / Al and the emitting layer was a LB film of the $Cd(HQ)_2$ amphiphilic complex with different numbers of layers. The emitting area was 2 × 3 mm^2. The luminance of the EL devices was measured with a luminancemeter as described early.[9]

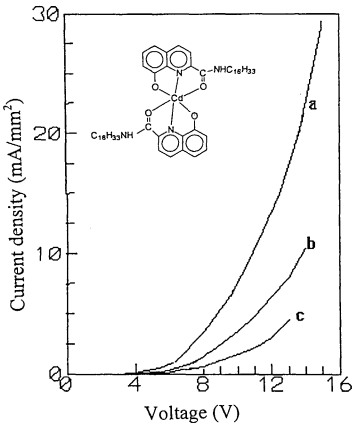

Figure 1. The relationship of current density and voltage in EL cells with emitters of $Cd(HQ)_2$ LB film. a) 9-layers, b) 15-layers, c) 21-layers. The inset shows the molecular structure of amphiphilic complex $Cd(HQ)_2$.

Figure 1 shows the relationship of current destiny (I) and voltage (V) in the EL devices. The shapes of the I-V curves are strongly dependent on the thickness of the LB films of $Cd(HQ)_2$ (luminance layer). With increasing LB film layers, the driving voltage increased. The driving voltages for the devices with an emitter of 9-, 15- and 21-layer LB films are 6, 7 and 8 V, respectively. The I-V curves can be fitted to an injection-limited model where the electron current is limited by electron injection from the cathode into the $Cd(HQ)_2$ LB film layer.[2]

A stable greenish-yellow emission with a luminance of about 1200 cd/m^2 was achieved and the luminance was proportional to the injection current in the region of 0.3-4.2 mA/mm^2. The luminance-current density characteristics of the EL device with an emitter of 15-layer LB film are shown in Figure 2.

The thickness of luminescent layer (LB films) drastically influences the emission of the electroluminescence devices. The luminance for the device with 15-layer LB film is higher than that with 9- and 21-layer LB films. That is, the emission efficiency of the EL device with 15-layers LB film (37.5 nm) was larger than those with 9- (22.5 nm) and 21-layers (52.5 nm) LB films. It can be interpreted that the luminance (B) is directly proportional to the carrier (electron and hole) concentration (n_e and n_h) and the electron-hole radiative recombination probability (γ):[9]

$$B \propto \gamma \cdot n_e \cdot n_h \quad \text{.....(1)}$$

When $Cd(HQ)_2$ LB films were used as an emitter, the recombination zone is located within about 4-layers of the LB films (*ca.* 10 nm) adjacent to the ITO to a distance of about (5-

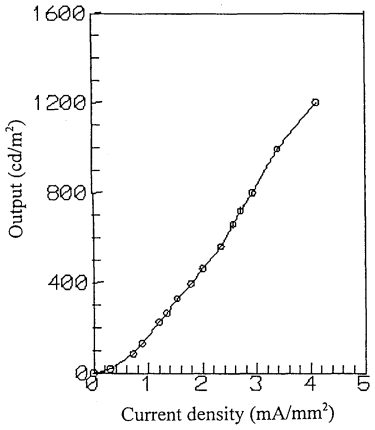

Figure 2. The relationship of output and current density in EL cells with an emitter of 15-layers $Cd(HQ)_2$ LB film.

6)-layers LB films (*ca.* 12.5-15 nm).[17] In the EL device with 9-layers LB films, the electrons injected from the Al electrode were quickly passed through the recombination zone; and in the EL device with 21-layers LB films, the number of electrons reached recombination zone was decreased because of their energy lose caused by the long-distance transporting procedure. That is, the γ and n_e in both the causes were decreased. Only to the EL device with (15-18)-layer LB films, there is possibility that not only γ but also n_e increases. Thus the EL intensity could be enhanced according to eq.(1)

The wavelength (490 nm, in Figure 3) of this emission was determined at a current density of 3.5 mA/mm^2. Comparison of the EL emission spectrum of the device with the PL spectrum of 15-layer $Cd(HQ)_2$ LB films[17] showed that the spectra do not greatly change. The PL and EL peak wavelengths and the half values of these two spectra are 480, 490 nm and 160, 220 nm, respectively. The EL emission spectrum was independent of the driving voltage and current. This result further indicates that the radiative recombination of injected electrons and holes takes place in the $Cd(HQ)_2$ LB films.

Comparing the performance of the $Cd(HQ)_2$ LB film with

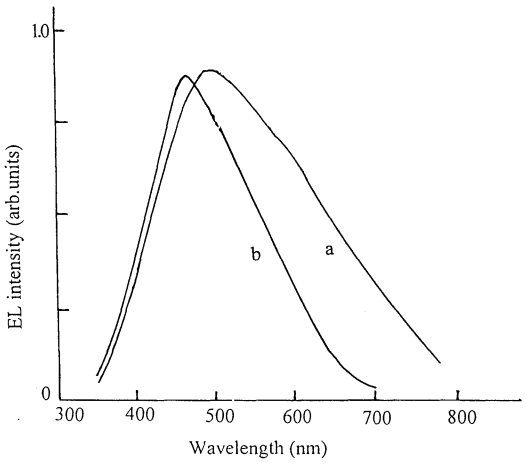

Figure 3. Photoluminescence (PL) and Electroluminescence (EL) spectra: a) EL spectrum of an ITO/$Cd(HQ)_2$ /Al device, b) PL spectrum of $Cd(HQ)_2$ LB films.

Table 1. Experimental Values for the Performance of the EL Devices

emitter of EL device	15-layer LB films	amorphous films
voltage (V)	10.0	10.0
emitting area (cm^2)	0.06	0.06
thickness of emitter (nm)	37.5	40
thickness of aluminum (nm)	500	500
deposition rate for film (nm/s)		0.4
dipping speed of LB films (mm/min)	3.0	
vacuum for film deposition (Torr)		10^{-5}

those of the amorphous $Cd(HQ)_2$ film prepared by spin coating at the same voltage, the luminance for the $Cd(HQ)_2$ LB films is about 2.3 times stronger than that for the amorphous $Cd(HQ)_2$ films of the same thickness (*ca.* 40 nm) prepared by a spin coating, and the EL spectra are the similar each other. It indicates that the ordered arrangement of the molecules can enhance the emission efficiency of luminescent material. The experimental values for the performance of the EL devices prepared herein was summarized in Table 1.

In conclusion, this device has unique characteristics of low voltage drive (about 7 V, for 15-layer LB films) and simplicity of fabrication. A more thorough investigation such as the fabrication of multilayer organic thin film EL devices with hole transporting material and electron transporting material are in progress.

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References

1 Y.Hua, J.Peng, D.Cui, L.Li, Z.Xu, and X.Xu, *Thin Solid Films,* **210-211,** 21 (1992).
2 C.W.Tang and S.A.VanSlyke, *Appl.Phys.Lett.,* **51**(12), 913 (1987).
3 C.W.Tang, S.A.VanSlyke, and C.H.Chen, *J.Appl.Phys.,* **65**, 3610 (1989).
4 Y.Hamada, T.Sano, M.Fujita, T.Fujii, Y.Nishio, and K. Shibata, *Jpn.J.Appl.Phys.,* **32**, L514 (1993).
5 P.L.Burn, A.B.Holmes, and A.Kraft etal., *Nature,* **356**, 47 (1992).
6 C.Adachi, S.Tokito, T.Tsutsui, and S.Saito, *Jpn.J.Appl. Phys.,* **27**, L713 (1988).
7 J.H.Burroughes, D.D.C.Bradley, and A.R.Brown, *Nature,* **347**, 539 (1990).
8 J.Kido, K.Nagai, Y.Okamoto, and T.Skotheim, *Appl.Phys. Lett.,* **59**, 2760 (1991).
9 G.Wang, C.Yuan, H.Wu, and Y.Wei, *Jpn.JAppl.Phys.,* **34**, L182 (1995).
10 F.L.Carter, "Molecular Electronic Devices I", Dekker, New York (1982).
11 M.Schmelzer, S.Roth, and C.P.Niesert, *Thin Solid Films,* **235**, 210 (1993).
12 J. Ouyang, Z.Tai, and W. Tang, *J.Mater.Chem.,* **6(6)**, 963(1996).
13 J.Ouyang, Z.Tai, and C.Jiang, and W.Tang, *Spectroscopy Letters,* **29(5)**, 763 (1996).
14 J.Ouyang, Z.Tai, and W.Tang, *Thin Solid Films,* **289**, 199(1996).
15 J.Ouyang, Z.Tai, and W.Tang, *Molecular Engineering,* **6**, 291 (1996).
16 T.J.Peng, Y.Hua, X.Xu, and A.Lu, *Chinese J.luminescence,* **15(1)**, 9 (1994).
17 The fluorescence of the complexes of HHQ and the details about the emission zone of the EL devices will be described elsewhere.