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IMPROVED STABILITY OF MOLECULAR ORGANIC EL DEVICES

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Abstract: Influence of emission sites on emission efficiency and running durability of molecular organic electroluminescent devices was investigated. When fluorescent dye rubrene was doped into TPD diamine hole transport layer, rubrene molecule emitted bright yellow light with a max. luminance of 61 000 cd/m^2. The device had the highest efficiency of 9.8 lm/W at 100 cd/m^2. Half-decay time of the device from initial luminance of 530 cd/m^2 under constant direct current was 3 600 h. On the other hand, when rubrene was doped into $BeBq_2$ complex electron transport layer, the efficiency was 4.4 lm/W and the half-decay time was 110 h. Thus doping site is found to exert significant influence both on the emission efficiency and the running durability.

INTRODUCTION

Organic electroluminescent devices (OELDs) have been expected to serve as a new type of flat-panel color displays since C.Tang and S.VanSlyke announced their first OELD (Ref. 1). Their success was based on a bilayer device which had an emitting electron transport layer (ETL) and a hole transport layer (HTL). They also reported a dye doped system in which a very small quantity of organic fluorescent dye was doped into a host ETL as emitter (Ref. 2). Tang's group used tris(8-hydroxyquinolinate)aluminum (Alq_3) as a host ETL, and various fluorescent dyes as dopants. The main virtue of doped systems are high emission efficiency. Wakimoto et al. achieved remarkable high luminance close to 10^5 cd/m^2 by doping of quinacridone in Alq_3 ETL (Ref. 3). In conventional doped systems, dyes were doped into ETL, but there are another possibility of doping site.

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We have examined new type of doped systems using doped HTLs instead of ETLs (Ref. 4,5). In this study the influence of emission sites on emission efficiency and running durability of molecular OELDs was investigated.

RESULTS AND DISCUSSION

Devices and Experiments

Figure 1 shows the molecular structures used in this study. N,N'-diphenyl-N, N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and bis(10-hydroxybenzo[h] quinolinato)beryllium ($BeBq_2$) were used as host materials. 4,4',4''- tris(3-methylphenylphenylamino)triphenylamine (MTDATA) reported by Shirota et al. (Ref. 6) was used for HTL. MTDATA and TPD were synthesized by Ullmann reaction (Ref. 7). Alq_3 and $BeBq_2$ were synthesized according to our previous reports (Refs. 8,9). 5,6,11,12-tetraphenylnaphthacene (rubrene) was commercially available. All materials were purified by train sublimation (Ref. 10).

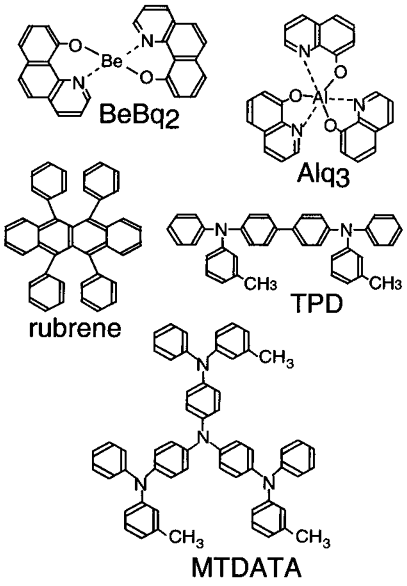

Fig. 1. Structures of EL materials.

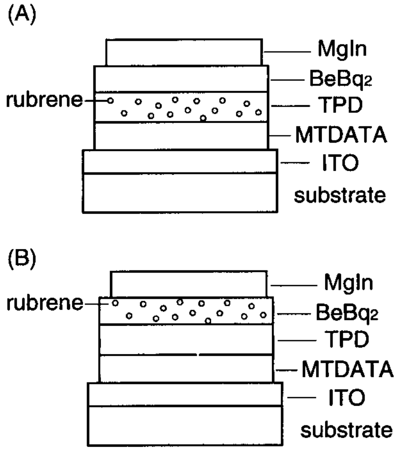

Fig. 2. Structures of devices A and B.

EL devices were fabricated by vacuum deposition at 1×10^{-4} Pa. The device structures were as follows.

device A : MgIn / $BeBq_2$ / TPD+**rubrene** / MTDATA / ITO
device B : MgIn / $BeBq_2$ + **rubrene** / MTDATA / ITO
device C : MgIn / $BeBq_2$ / TPD / MTDATA / ITO
device D : MgIn / Alq_3 / TPD + **rubrene** / MTDATA / ITO

Figure 2 shows the structures of devices A and B. The suitable doping site, whether an ETL ($BeBq_2$) or a HTL (TPD), was examined by comparing devices A and B. Undoped device C was used for a reference. Devices A and D were compared to determine whether Alq_3 or $BeBq_2$ is superior for ETL.

The thickness of layers was as follows: $BeBq_2$ or Alq_3 (50nm), TPD (40nm), MTDATA (60nm) and MgIn (200nm). The doping concentration of rubrene was 5 wt.-% against host material. The weight ratio of MgIn alloy was 10 to 1. The emission area was 2x2 mm^2. The photoluminescence (PL) spectra of organic thin films(100 nm) were measured with a fluorescence spectrophotometer. The ionization potential of these films were measured with an atmospheric low energy electron counter (Riken AC-1). All measurements were carried out in dry air at room temperature.

Light Emitting Performance

The maximum luminance, the luminance at 10 mA/cm^2 and the light emission efficiency at 100 cd/m^2 of devices A-D are summarized in Tab. 1. Device A had the highest luminance of 61 000 cd/m^2 and the highest emission efficiency of 9.8 lm/W. From the comparison of devices A and B, the most suitable doping site of rubrene is found not the ETL ($BeBq_2$), but the HTL (TPD). Comparing the efficiency of devices A and D, it is also concluded that $BeBq_2$ is superior to Alq_3 as an ETL.

Tab.1. Summary of the emitting performance.

device	Max. luminance (cd/m^2)	Luminance @10mA/cm^2 (cd/m^2)	efficiency @100cd/m^2 (lm/W)
(A) rub-TPD	61 000	1 000	9.8
(B) rub-BeBq2	14 000	510	4.4
(C) undoped	22 000	690	4.0
(D) Alq3	54 000	940	6.2

Running Durability

Figure 3 shows the running test results of devices A-D in dry air under the condition of constant direct current. The initial luminance of these devices was set at around 500 cd/m^2, which is a typical luminance of conventional displays. The lifetimes or the half-decay times of these devices, in which luminance was reduced to a half, were as follows: device A (3554 h), device B (110 h), device C (23 h) and device D (1150 h). Device A had the longest lifetime of all. From the comparison of devices A and B, not only in emitting performance, but also in running durability, the most suitable doping site of rubrene is concluded to be the HTL (TPD).

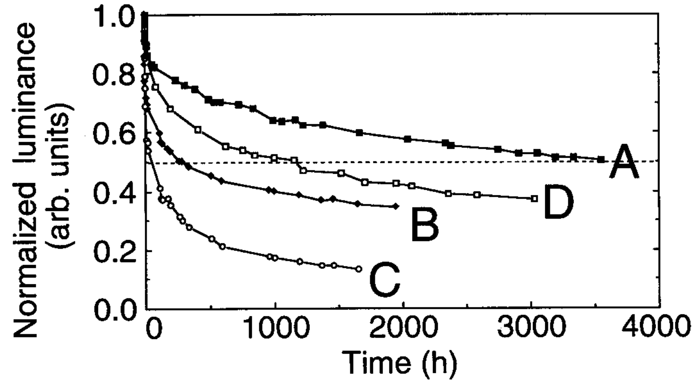

Fig. 3. Running test results of devices A-D under constant currents.

The emmission efficiency at various luminance is summarized in Tab. 2. Device A had superior efficiency to the others at all luminance. Improved stability of device A can be explained by this fact.

Tab. 2. Emission efficiency at various luminance.

device	efficiency @ 300cd/m^2 (lm/W)	efficiency @ 500cd/m^2 (lm/W)	efficiency @ 1 000cd/m^2 (lm/W)
(A) rub-TPD	7.7	6.7	5.3
(B) rub-BeBq2	3.2	2.7	2.0
(C) undoped	3.4	3.3	3.0
(D) Alq3	5.0	4.4	3.7

The efficiency was in the order of A > D > C > B, however, the lifetime was in the different order of A > D > B > C. Therefore in the case of devices C and D, the lifetime might be controlled by another factor rather than emission efficiency.

The running test results of the best device A under various current density are shown in Tab. 3. The luminance decay became very slow under low drive currents. The lifetime longer than 18 000 h or 2 years were obtained from the initial luminance of 56 cd/m^2.

Tab. 3. Running test results of device A under various current density.

Current density (mA/cm^2)	Initial luminance (cd/m^2)	lifetime (h)
0.5	56	>18 000 (60%)
1.0	110	17 000
2.0	220	8 800
5.0	530	3 600
10.0	1 000	680

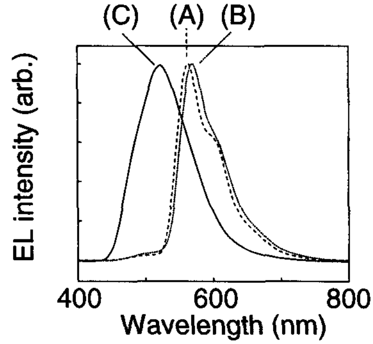

Fig. 4. EL spectra of devices A-C.

Recombination Process

Figure 4 shows the EL spectra of devices A-C. The emission color of devices A and B were yellow, and the peaks were 562 nm and 567 nm, respectively. Since PL peak of rubrene is also 562 nm, origin of these emissions are attributed to excited states of rubrene. On the other hand, device C emitted green light and the peak was 516 nm. This emission is attributed to BeBq$_2$.

Figure 5 shows the energy band diagrams and recombination process in devices A and C. In device C, electron transfer from BeBq$_2$ to TPD is thought to be difficult because of the large energy barrier of 0.6 eV at the interface between TPD and BeBq$_2$. Therefore recombination occurs in BeBq$_2$. On the other hand, in device A, electron transfer from BeBq$_2$ to rubrene is very easy because there is no energy barrier at the interface between rubrene in TPD layer and BeBq$_2$. In device A, as the result of recombination in rubrene molecule, rubrene is excited directly. This is thought to be the reason for the extra high efficiency and the longest lifetime of device A.

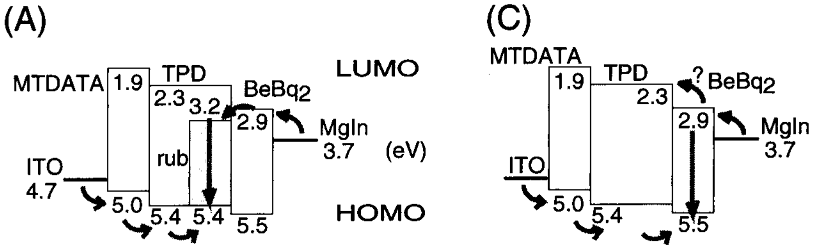

Fig. 5. Recombination process in device A and C.

CONCLUSION

Based on the new type of doped structure we have developed, running durability of molecular OELDs was improved and high emission efficiency of 9.8 lm/W at 100 cd/m^2 was obtained. Doping site is found to exert significant influence both on the emission efficiency and the running durability of molecular OELDs. However, the most suitable doping site will depend on dopants. Therefore choosing appropriate set of dopant and host material to reduce energy barriers at organic interfaces is very important.

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