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DESIGN OF ORGANIC ELECTROLUMINESCENT MATERIALS AND DEVICES

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Abstract: Multilayer organic light emitting devices were studied with an aim of achieving highly efficient emission. It was shown that organic fluorescent materials had advantages in achieving very high efficiency of outer emission, more than 5 lm/W, and in blue-emitting materials. Three layer devices which had double hetero-junctions between two different organic layers were studied with an objective of accomplishing confinements of injected carriers and generated excitons within the emission layer. For the former purpose, requirement for the relation between the electronic energies in the carrier transport layer and those in the emission layer was clarified. The requirement for confinement of the excitons was also demonstrated from the excitation energy point of view.
The emphasis was laid on the size effects in three layer EL devices. Variation of the fluorescent lifetime or the radiative decay rate with the spacing between the emission layer and the metallic electrode was discussed theoretically and experimentally. It was demonstrated that enhancement and suppression of the spontaneous emission from the excitons occured periodically with variateion of the spacing. Variations of EL intensity and pattern of outer emission through semitransparent glass substrate with the spacing were discussed also.

Keywords: electroluminescence, multilayers, excitons, injection, space charge, charge transport, recombination, fluorescence

INTRODUCTION

The principle of the organic electroluminescent (EL) devices is quite similar to that of inorganic light emitting diodes (LED). The fundamental processes for emitting light are

1) injection of electrons and holes into an emission layer (EML).

2) recombination of the injected carriers in the EML.

3) creation of molecular excitons by the recombinations.

4) radiative decay of the excitons in the EML.

To assist the carrier injections, one often used an electron transport layer (ETL) and/or a hole transport layer (HTL) in the EL devices and proposed three types of multilayer device so far. The proposal of the multilayer structures brought about an abundant choice of the fluorescent dyes for the EML and then strong emission of any color from blue to red. We will discuss the following subjects in this paper, with an aim of achiev-

ing more efficient light emission:

1) materials design for achieving high efficiency of light emission,

2) confinement of the injected carriers within EML,

3) confinement of the molecular excitons within EML,

4) control of spontaneous emission from EML,

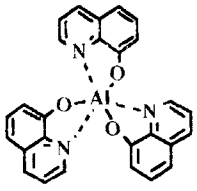
5) control of outer emission pattern from the EL device.

MATERIAL DESIGN FROM HIGHLY EFFICIENT ELECTROLUMINESCENCE

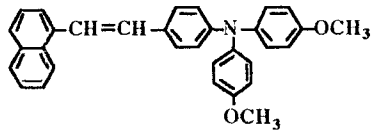
One of the most important requirements in fluorescent dyes for EML is to emit strong fluorescence in the solid thin films. Several kinds of fluorescent dyes, for instance 8-hydroxyquinoline-Al complex (AlQ_3), a naphthostyryl derivative (NSD) and so on, fulfil this requirement. Even in these molecular solids, however, a concentration quenching effect can not be avoided to some extent. Doping with a small amount of another fluorescent dye into the EML is well worth of investigation. The doping effect was studied in multilayer EL devices with an EML composed of AlQ_3 doped with a quinacrydone derivative (QCD) which has very high efficiency of fluorescence in a dilute solution. The EL intensity was found to be dependent on the concentration of the dopant and became higher than that of undoped AlQ_3 EML, within the concentration range up to 2 %. The EL was confirmed from the dopant molecules by the measurement of the EL spectrum. The dopant concentration of 0.47 % gave the highest result. The value of luminance was 68000 cd/m^2 at a current density of 1 A/cm^2. This result corresponds with an outer emission efficiency of about 5 lm/W.[1] These devices are regarded as the more efficient light emitting devices, compared with commercially inorganic LED.

Organic fluorescent materials have the advantage in application to blue emitting devices over the inorganic materials. Several dyes were proposed so far for this application. For instance, several kinds of oxadiazole derivatives were studied for this purpose. We found that four oxadiazole derivatives at least emitted strong blue light of 1000 cd/m^2 at 100 mA/cm^2. An example of the derivative is PBD-2 shown in Figure 1. PBD-2 had been synthesized originally in the course of study for avoiding recrystallization of amorphous thin films of simple oxadiazole derivative (PBD-1), which had been used as an ETL material.

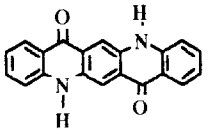
The organic materials used in our study are shown in Figure 1.



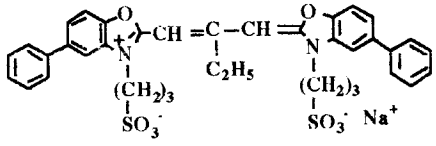
AlQ_3



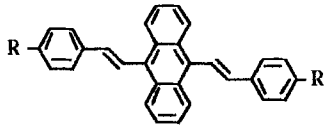
NSD



QCD



OCD

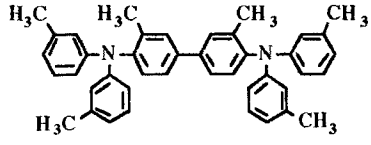


BSA

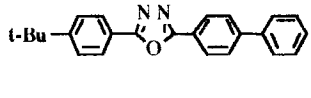
-1: R =-CN

-2: R =-NPh 2

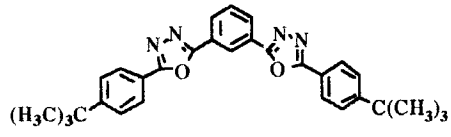
-3: R =-NEt 2



TAD



PBD-1



PBD-2

FIGURE 1 Orgnaic materials used in the present study

DISTRIBUTION OF EMISSION SITES IN THE EMISSION LAYER

A specific zone in the EML can be doped with a small amount of other fluorescent moleculaes which have lower excitation energy than that of EML host molecules. If the

excitons in the specific doped zone are created by the carrier recombination, one can detect the EL spectrum from the dopants excited due to the energy transfer from the excitons of the host molecules. Then one can determine the location of the emission sites in the EML by adopting the doping method in which an extremely thin doped zone is formed at a specific depth from the interface between the EML and the carrier transport layer.

The distribution of the emission sites in the EML was evaluated experimentally at a current density of 100 mA/cm^2 in two layer devices (ITO/EML/ETL/MgAg and ITO/HTL/EML/MgAg) and a single layer device (ITO/EML/MgAg). In the two layer devices, it was found that the emission sites were located from the interface between two organic layers to a few tens nm and their distributions were fairly wide. In the single layer device, the emission sites were distributed in much wider region.[2] In every case, there were no emission sites in the region from the outer electrode (ITO or MgAg) to a depth of about 25 nm.[2] Following reasons for the results on the distribution of emission sites should be taken into acount;

1) Lack of blocking characteristics to carrier flow into outer electrode without recombination, in other words, failure in confinement of the injected carriers within EML.
2) Non-radiative decay of the excitons created near the metallic electrode due to energy transfer into the metal.
3) A considerable portion of the emission from the excitons near ITO electrode may be transformed into evanescent waves in ITO layer with higher refractive index than EML and may not contribute to the outer emission.[3]

In a series of two layer device (ITO/EML/ETL/MgAg), we measured the luminance at a fixed current density of 100 mA/cm^2 as a function of the thickness of EML. When the thickness decreased below 30 nm, the luminance decreased drastically with decrease of the thickness.[4] This behavior suggests that the above factors play an important role in the emission.

MATERIAL DESIGN FOR CONFINEMENT OF CARRIERS AND EXCITONS WITHIN THIN EMISSION LAYER

In order to attain highly efficient EL, it is extremely important to confine the injected electrons and holes within a thin EML and to increase the possibility of their recombination. To understand the carrier injection and blocking characteristics across a hetero-junction between two semiconducting layers, it is very useful to analyze the carrier transport by

using the elctronic band diagram. In spite of the amorphous nature in organic thin films, we tried to discuss the carier injection and blocking in terms of the ionization potential and the electron affinity of the organic thin film. The ionization potential I_p of the organic film was determined from the measurements of photoelectron emission and the value of electron affinity E_a was assumed to be difference between I_p and the optical absorption edge in the electronic spectrum of the thin film. The values of I_p and E_a for several EML as well as for representative carrier transport layers are listed in Table 1, where BSA is a 9,10-bisstyrylanthracene derivative, NSD is a naphthostyryl derivative, OCD is a cyanine dye, TAD is an aromatic amine dimer and PBD is an oxadiazole derivative.

TABLE 1 Electronic energies in thin films used for organic EL devices

Thin Film		I_p(eV)	E_a(eV)	E*(eV)
EML	BSA-1	6.0	3.5	2.21
	BSA-2	5.5	3.1	2.16
	BSA-3	5.4	3.0	2.03
	NSD	5.5	2.8	2.30
	OCD	5.4	3.2	2.23
HTL	TAD	5.5	2.4	2.88
ETL	PBD	5.9	2.6	3.10
Cathode	MgAg	3.7		
Anode	ITO	4.9		

According to a simple consideration, the following inferences are drawn;

1) The ETL should have a large I_p for blocking the hole flow out of EML and a large E_a for assisting the elctron injection from MgAg.
2) The HTL should have a small I_p for assisting the hole injection from ITO and a small E_a for blocking the electron flow out of EML.

The luminance-current characteristics for several kinds of multilayer device demonstrated that the above predictions were valid.

It is extremely important to confine the molecular excitons within EML also. A three layer device (ITO/HTL/EML/ETL/MgAg) is favorable for this purpose. The requirement for the carrier transport layers is that their excitation energies, E*, should be higher than that of the EML, since the energy transfer from the EML to the carrier transport layers should be avoided. Then, material design for effective confinements of the injected carriers and the created excitons within EML should be done in accordance with the conclusion shown below;

$$I_p(ITO) \lesssim I_p(HTL) \simeq I_p(EML) \ll I_p(ETL)$$
$$E_a(HTL) \ll E_a(EML) \simeq E_a(ETL) \lesssim I_p(MgAg)$$
$$E^*(HTL) > E^*(EML) < E^*(ETL)$$

If these requirements are fulfilled, the confinement of carriers and excitons could be attained even within the OCD monomolecular layer.[5]

DEVICE DESIGN FOR HIGHLY EFFICIENT EMISSION

Control of Spontaneous Emission Through Designing The Optical Micro-cavity Composed of Three Layer EL Device

Remembering that a three layer EL device has a thickness less than the wavelength of the emitted light that an extremely thin EML is sandwiched by a couple of metallic electrode and the carrier transport layers, one can recognize that this device corresponds to a kind of optical micro-cavity. When a molecular exciton is placed between two parallel metallic mirrors whose spacing is close to the wavelength of light, the emission from the exciton cannot beirreversible any more. One should consider the interaction of emitted light with confined radiation field arround the exciton. In this micro-cavity, enhancement and suppression of the spontaneous emission from the excitons is expected to occur.

We observed the fluorescent lifetime as a function of the spacing **d** betwen EML and the mirror (MgAg electrode) and found that the fluorescent lifetime changed remarkably with variation of **d**. We found that the fluorescent lifetime at a specific **d** was shorter and that at another specific **d** became longer than the lifetime of the fluorescent thin film without the metallic mirror.[6]

To understand the fluorescent lifetime as a function of the spacing **d**, we assume that the decay processes of the created excitons are composed of three different processes;

1) radiative decay which yields fluorescence,

2) non-radiative thermal decay,

3) non-radiative decay due to the energy transfer into the metallic mirror.

Then, total decay rate which corresponds with inverse of the fluorescent lifetime is given by the sum of the three decay rates. By appling Chance's theory to the above model, we can interprete the observed wave-like variation of the lifetime with **d**.

We should point out that the minima and the maxima in the lifetime against **d** curve appear at the spacing of $(2n-1)\lambda^*/4$ and $2n\lambda^*/4$, respectively, where λ^* is effective wavelength and is given by emission-peak wavelength λ devided by the refractive index of the organic medium. It should be stressed also that the non-radiative decay

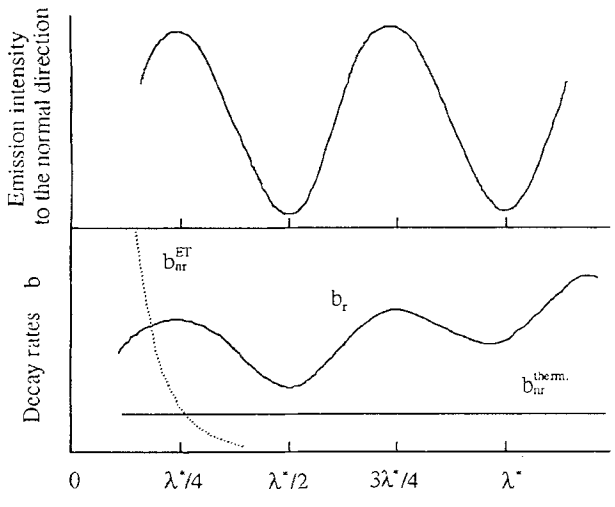


FIGURE 2 Micro-cavity effects on the exciton decay rates and the outer emission intensity. b_r, b_{nr}^{therm}, b_{nr}^{ET} mean the rates of radiative decay, non-radiative thermal decay and non-radiative decay due to the energy transfer into the mirror, respectively

process due to the energy transfer into the metallic mirror becomes prodominant in the range of **d** below 50 nm.

A schematic representation for the variations of the decay process as well as emission intensity are shown in Figure 2.

Interference Effects In Three Layer EL Device

A second effect expected to occur in the micro-cavity is an interference effect of the emitted light. Only a portion of the emitted light from the molecular excitons placed in front of two mirrors is transmitted directly into outer space through a semi-transparent ITO. Remaining portions of the emission are transmitted through ITO after repeated reflections or along the glass substrate. Therefore, the shape of the outer emission pattern is expected to be changed with variation of the thickness or dimension of the three layer EL device.

We measured the intensity of EL emission at a fixed current of 100 mA/cm^2 as a function of the spacing **d** between EML and MgAg electrode. The luminance changed remarkably with variation of **d** and became a maximum at **d** of around 70 nm.

To understand the variation of the luminance with **d**, we adopted a simple model like a Fabry-Perot cavity structure in which the EML is represented by vibrating dipoles

without thickness. The amplitude of the transmitted light directly into outer space can be calculated by using the transmittance of the glas substrate. The amplitude of the transmitted light after multiple reflections can be calculated by using the above factor and the reflectances of the glass substrate and the MgAg electrode. Then, the variation of the observed luminance and the outer emission pattern can be interpreted through the calculation of the intensity of the outer emission by using the above model. Again we should stress that the maxima of the emission of perpendicular direction to the EL device surface appear at the spacings of $(2n-1)\lambda^*/4$.

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