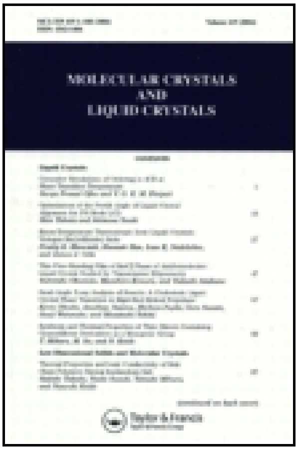

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Material Developments and Light Control in Organic Light-Emitting Diode

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We report the influence of organic materials on the thermal stability and emission efficiency of organic light-emitting diode (OLED). To improve the device performance several hole transporting materials and emitting materials were developed based on triphenylamine and metal-chelate complex, respectively. The electroluminescent characteristics of the OLEDs are shown and discussed in view of properties of the materials. Control of light emission in the OLED with microcavity is also presented to suggest a new application.

INTRODUCTION

Light-emitting diodes (OLEDs) based on organic materials such as small molecules and polymeric materials are attracting much attention as candidates for flat-panel displays and backlights for liquid crystal displays.[1,2] Over the past ten years a considerable number of researches have been made on the development of new materials to improve the device performances.[3] A half-decay lifetime of more than 10000 h from an initial brightness has been already realized in several emitting materials, and more recently, a practical display has been commercialized.[4] However, further improvements of the lifetime and the color tunability are needed to realize reliable full-color displays. Other applications only possible in the OLED are also important to stimulate the OLED research field..

In this paper, we review the material developments for hole-transport layer and emitting layer, and the control of light emission in the OLED. To improve the thermal stability and emission efficiency, it would be suggested that the hole transporting materials are based on aromatic amine and the emitting materials are based on metal-chelate complex structure. The emission characteristics of the OLED with microcavity are also shown for an application to the liquid crystal (LC) projector.

HOLE TRANSPORTING MATERIALS

The representative OLED structure consists of two organic layers for a hole transport and a light emission. The most well-known emitting material is tris (8-quinolinolato) aluminum (Alq3) reported by C. Tang et al..[1] The durability of Alq3 based device isrelated to the thermal stability of the hole-transport layer.[5] Several triphenylamine oligomers were synthesized (Fig.1) and systematic experiments of the temperature dependences of EL characteristics were carried out in the OLEDs using trimer (TPTR), tetramer (TPTE), pentamer (TPPE) and a well-known dimer (TPD) for the hole-transport layer[6,7] The linear linkage of triphenylamine resulted in a rise of glass transition temperature (Tg). Hole mobility of the TPTE was also measured by a conventional Time-of-Flight technique and found to be 3×10^{-3} cm^2/Vs which is higher than that of TPD. This indicates the excellent hole transporting ability of TPTE.

The device using TPD exhibited a drastic drop of the EL output at 70 °C. This temperature is called as a critical temperature hereafter and shows a good correspondence with Tg (60 °C). The critical temperatures for other devices were 110 °C for TPTR, 135 °C for TPTE and 155 °C for TPPE. Figure 2 shows the relation between Tg and the critical temperature. The linear relationship indicates that the thermal stability of the devices with Alq3 emitting layer is dominated by the hole-transport layer. [8] The device using TPTE showed a half-decay lifetime of 100 h at 100 °C under a driving condition of 11mA/cm^2. Recently, long operating lifetimes in excess of 200 h have been achieved at 105 °C at a luminance of 300 cd/m^2 in the quinacridone doped Alq3 devices using TPTE.

Even at room temperature, if the device is driven at a high current or a high luminance the lifetime is influenced by the hole transporting material. Compared with α-NPD (Tg=95 °C) and TPD (Tg=60 °C), the device using TPTE (Tg=130 °C) exhibited a longer lifetime at a driving current of 110 mA/cm^2: 22 h for TPTE, 8 h for α-NPD and 5 h for TPD. This result is attributable to a rise of device temperature by the Joule-heat.

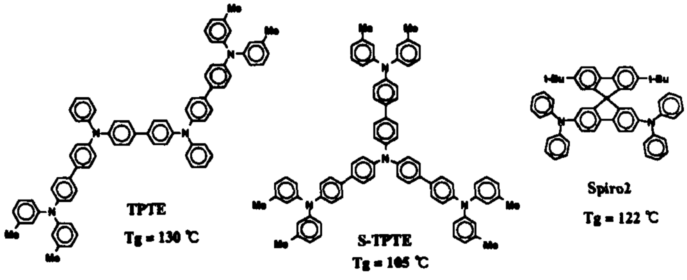

FIGURE 1 Novel hole transporting materials

We have also investigated the influence of hole transporting material on the emission efficiency of the Alq3 based device. Several hole transporting materials have been used in the Alq3 based device. Significant influence was found on the EL efficiency.[9] The highest efficiency at a luminance of 300 cd/m^2 was obtained in the device using a novel compound, Spiro2 (Fig.1); photometric efficiency of 6.1 cd/A and quantum efficiency of 2.1 % photon/electron. These efficiencies are higher than those reported in the Alq3 based devices using other hole transporting materials.[1,8] The difference is primarily attributable to suppression of the exciplex formation at the interface of the Alq3 layer and the hole-transport layer.

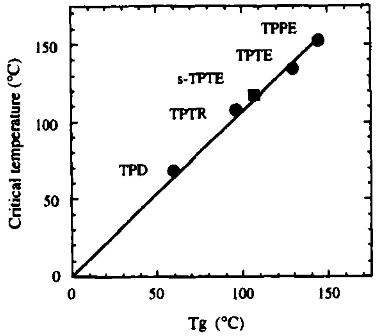

FIGURE 2 Relationship between Tg of hole-transport material and thermal stabity of Alq3 based device.

EMITTING MATERIALS

The well-known Alq3 is one of metal-chelate complexes. From earlier researches, the metal-chelate complex is believed to be a promising structure for an efficient emitting material.[10] Novel metal-chelate complexes were synthesized (Fig.3) and the EL characteristics were investigated in the OLEDs consisting of hole-transport layer and emitting layer.[11,12] These complexes have either polycyclic aromatic or fused ring ligands which coordinate to zinc or aluminum.

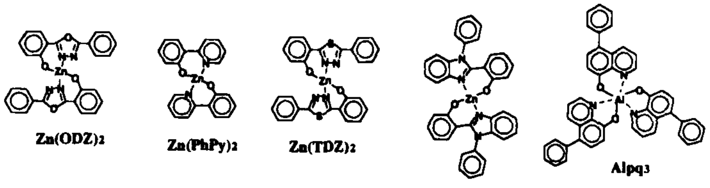

FIGURE 3 Novel metal-chelate complexes.

Visible light emission was observed at a voltage of 3 - 4 V and its intensity reached one thousand cd/m^2 at a voltage of 7 - 13 V, and some devices showed a maximum luminance in excess of ten thousand cd/m^2. The emission wavelengths, colors and emission efficiencies are summarized in Table 1. The blue emitting device using $Zn(ODZ)_2$ exhibited an photometoric efficiency of 1.8 cd/A and a quantum efficiency of 1.5 % at a luminance of 300 cd/m^2, and the $Al(ODZ)_2$ device gave almost the same efficiencies as $Zn(ODZ)_2$ device. This implies that the difference in metal atom in the complex does not influence the EL efficiencies. The other blue emitting device using $Zn(BIZ)_2$ exhibited 2.0 cd/A and 1.5 % in photometoric efficiency and quantum efficiency, respectively. The quantum efficiencies of these blue emitting devices are high compared to those of the blue emitting devices using distyryl arylene derivatives.[13] The $Alpq_3$ provided a photometric efficiency of 2.4 cd/A and a quantum efficiency of 0.8 % in yellow emission, which is little lower than those of the Alq_3 based device. These results imply that the metal-chelate complexes have not only light-emitting ability but also electron transporting ability, as we expected in molecular design.

The $Zn(ODZ)_2$ was also used as a host material for doping of perylene. In the device with perylene doped $Zn(ODZ)_2$ layer, the energy transfer from $Zn(ODZ)_2$ to perylene was observed. The EL spectrum of the 3.4 % perylene doped device resembled a photoluminescence of dilute solution of perylene, and the quantum efficiency and the CIE coordinates were 1.6 % and (0.16, 0.18), respectively.

The device using $Alpq_3$ exhibited a long lifetime in excess of 500 h at a luminance of 300 cd/m^2. However, the devices using other zinc complexes exhibited poor lifetime. The reasons for such poor lifetimes are not clear. It may be related to the instability of the excited states of these compexes.

TABLE 1 EL characteristics of devices using various emitting materials.

E M	EL Peak (nm)	Color	Maximum luminance (cd/m^2)	Photometric * efficiency (cd/A)	Quantum * efficiency (%)
$Zn(ODZ)_2$	449	blue	11000 (18V)	1.8	1.5
$Zn(TDZ)_2$	508	bluish-green	4020 (12V)	2.4	0.8
$Zn(PhPy)_2$	485	greenish-blue	11450 (15V)	1.3	1.2
$Zn(BIZ)_2$	447	blue	4100 (13V)	2.0	1.5
$Alpq_3$	550	yellow	26000 (14V)	2.4	0.7
$Al(ODZ)_3$	447	blue	3500 (18V)	2.0	1.7

* at a luminance of 300 cd/m^2

CONTROL OF LIGHT EMISSION

The OLEDs are attractive for application to flat-panel displays with passive or active matrix. Further investigations concerning other applications only possible in the OLED are also important to stimulate the OLED research and development.

Recently, the OLEDs have been applied to the light sources of a liquid crystal (LC) projector and succeeded in the color projection, about 350 mm x 260 mm, on a screen.[14] The conventional LC projector consists of the LC valves providing video image and the optical system generating three primary color lights, and is attracting much attention to great demand for a large-size display with high resolution. From this new application of the OLEDs, it has been found that the compactness and lightness of the projector are surprisingly improved compared to the conventional LC projector. In the OLEDs, the microcavity structure is applied to control the light emission.[12] The device structure of OLED with microcavity (MOLED) is schematically shown in Fig.4. In addition to the conventional OLED structure, the dielectric mirror (DM) is inserted between the glass substrate and ITO layer. The microcavity structure is defined by the top metal layer acting as mirror and the dielectric mirror.[15] For the metal mirror and the dielectric mirror, an Al layer and three pairs of SiO_2/TiO_2 quarter-wave layers were used, respectively.

In the Alq_3 based device, the forward directionality of light emission was achieved as well as spectral narrowing and intensity enhancement at a resonant wavelength. [16] The theoretical emission spectrum in the forward direction can be calculated based on the classical optics. Figure 5 shows the emission spectra of three MOLEDs for each primary color.[17] The resonant wavelengths, 618 nm for the red MOLED, 537 nm for the green

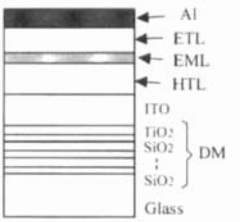

FIGURE 4 Structure of a microcavity OLED. HTL, EML and ETL are hole-transport layer, emitting layer and electron-transport layer .

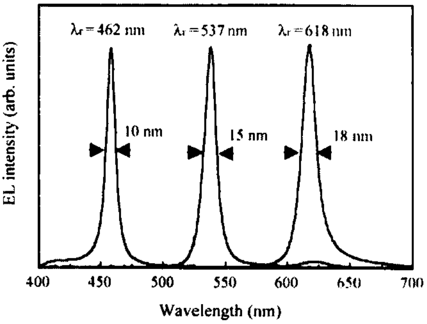

FIGURE 5 EL spectra of microcavity OLEDs for primary three colors.

MOLED and 462 nm for the blue MOLED were obtained. The halfwidths of these RGB emission spectra were 18 nm, 15 nm and 10 nm, respectively. Color purification is one of advantages in the MOLED. Further improvement is easy by tuning the resonant wavelength and varying the spectral width. The enhancement of emission intensity at the resonant wavelength (spectral power density) was clearly observed in each MOLED. The measured enhancement ratio was 5 for the red MOLED, 2.7 for the green MOLED and 1.4 for the blue MOLED. The maximum luminance observed in the forward direction at a high operating voltage was 10^3 -10^4 cd/m^2.

All the microcavity devices exhibited the strong directionality in the forward direction, especially in the green MOLED the strongest directionality was observed. The emitted light is concentrated in a certain range of solid angle centered at the normal axis to the device surface. This is quite unique since the parallel light can be realized in a flat-panel type emitting device without using an optical lens. The microcavity device opens the door to new applications such as the LC projector.

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