



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and
subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Version of record first published: 04 Oct 2006.

To cite this article: Youngk Yoo Kim , Won Jei Cho , Chang Sik Ha , Tetsuo Tsutsui & Shogo Saito
(1996): Electroluminescence Properties of Dye-Dispersed Poly-Imide Multilayer Light Emitting
Diode (Led): (I) Absorption, Photoluminescence, and Structures, Molecular Crystals and Liquid
Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 280:1, 343-348

To link to this article: <http://dx.doi.org/10.1080/10587259608040354>

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ELECTROLUMINESCENCE PROPERTIES OF DYE-DISPERSED POLY- IMIDE MULTILAYER LIGHT EMITTING DIODE (LED): (I) ABSORPTION, PHOTOLUMINESCENCE, AND STRUCTURES

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Abstract In this article, the absorption and photoluminescence spectra of Alq3/poly(ether imide)(PEI) blend films are discussed, in order to get insights on the electroluminescence properties of the Alq3-dispersed PEI multilayer LED. The structure of the Alq3-dispersed PEI films was also investigated by optical microscopy with image processor.

INTRODUCTION

Recently, organic EL LEDs have attracted much interest because of their particular low driving bias voltage, low fabrication cost, ease of device design and possible control of emission band compared to inorganic EL LEDs.¹⁻³ One of typical organic EL LEDs has been known to consist of single or multilayer sublimed dyes and carrier transporting materials. Another types of EL LEDs are π -conjugated polymeric materials, that is, conducting polymers, such as poly(phenylene vinylene), poly(3-alkyl thiophene), and polyphenylenes.⁴⁻⁶ In addition to these types of LEDs, dye-dispersed polymer LEDs are

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also emerging EL LEDs, because polymers have an advantage of easy processability, intrinsically good durability, and outstanding flexibility.⁷⁻⁹ In case of dye-dispersed polymer EL LED, one of the significant requirements in the binder polymer is the thermal stability because of heat-generation during bias potential applied. This thermal stability is directly related to the life time of device. One of the best candidates as a thermally stable polymer is polyimide such as PMDA-ODA and BPDA-PDA, which has low moisture uptake, low solvent swelling, low thermal expansion coefficient, low dielectric constant, and good mechanical properties.

In the present study, poly(ether imide)(PEI) is used as a binder polymer, because PEI is soluble in a polar base solvent so that one can prepare a device easily from its solutions. PEI is also regarded as an appropriate binder polymer due to high glass transition temperature ($>215^{\circ}\text{C}$).¹⁰ Tris(8-hydroxyquinolino) aluminum, Alq3, is introduced as an emitting material. To improve the efficiency in carrier injection, triphenyl amine derivative(TPD) and butyl-PBD are also used for effective hole and electron injection.

The purpose of this article is to preliminarily investigate the absorption and photoluminescence spectra along with the structure of the Alq3-dispersed PEI films, prior to the electroluminescence properties of the resultant EL LEDs.

EXPERIMENTAL

Materials used in the present study were shown in Figure 1. Solution blends of Alq3 and PEI in N-methyl-2-pyrrolidinone (NMP) were prepared with the composition of 0/100, 5/95, 10/90, 20/80, 30/70, and 50/50 by weight percent. Since PEI is not so well soluble in a solvent at room temperature, heat below 60°C was applied to make a clear solution. After obtaining a clear PEI solution, a given amount of Alq3 was incorporated into the PEI solution, followed by subsequent mixing of the final mixtures for one day. Alq3 is completely solved just after about 5 to 10 min. The overall solid concentration is about 2wt.%. The solutions were casted onto non-fluorescent glass substrate and softbaked at 90°C . After ca. 2 hours, Alq3/PEI thin films, illuminating light green color owing to Alq3, were obtained. The film thickness is ranged from 100nm to 200nm.

UV-VIS absorption and photoluminescence spectra were obtained using UV-VIS spectrophotometer(UVIKON 860, KONTRON Co.Ltd) and fluorometer(SFM 25, KONTRON Co.Ltd). The structure of films was examined by the optical microscopy equipped with image processor(OLYMPUS-IMAGE-PRO). To make a LED device, the Alq3/PEI solution with and without carrier transporting materials were casted onto the

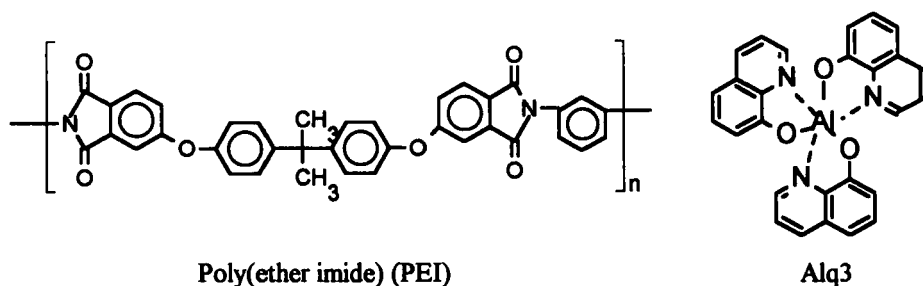


FIGURE 1 Binder polymer and emitting material used in the present study

precleaned ITO-glass etched in aqua solution. Several kinds of cathode electrode, e.g., Al, Ca, Ag, Mg:Ag(10:1), were vacuum-deposited on the organic emitting layer. The details of the procedure and results on the EL properties will be appeared elsewhere.

RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of Alq3 and PEI blend films with various compositions. PEI homopolymer shows absorption ranging from ca. 400nm (3.1eV) to

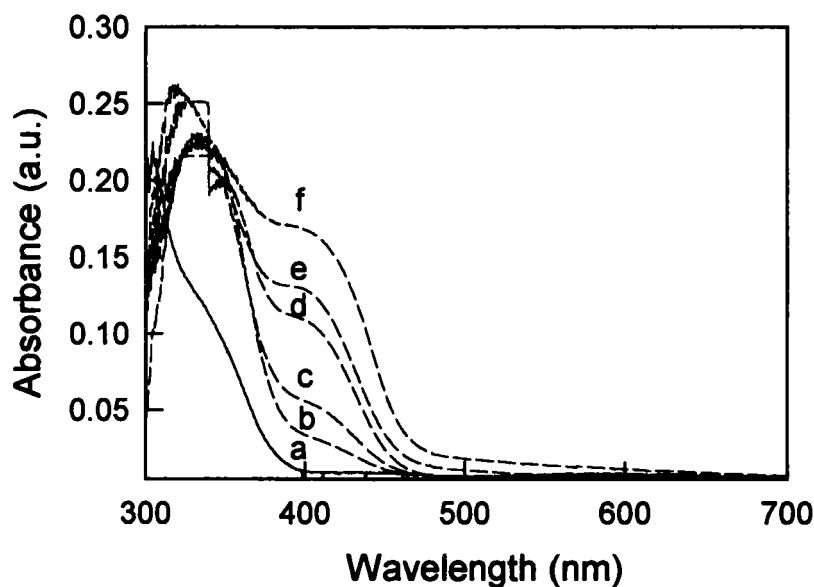


FIGURE 2 UV absorption spectra of Alq3/PEI blend films : (a:0/100, b:5/95, c:10/90, d:20/80, e:30/70, f:50/50)

higher energy region. This absorption is mainly due to phenylene groups in bisphenol-A unit and phthalimide group. In case of Alq3-dispersed PEI films, new absorption bands for Alq3 from 400nm to 475nm were occurred. Besides, the peak for maximum absorption of PEI was shifted to lower energy region, implying the generation of weak exciplex between the aromatic groups in PEI and Alq3 molecules. On increasing Alq3 contents, the absorption shoulder around 400nm was increased and the shape of PEI absorption was changed. It is noted from the spectrum of 50/50 Alq3/PEI film that the absorption intensity of PEI is higher than that of Alq3. The films above 30/70 composition showed hazy appearance, that is, phase separation was brought out between Alq3 and PEI. But the absorption shoulder of Alq3 was not changed with composition.

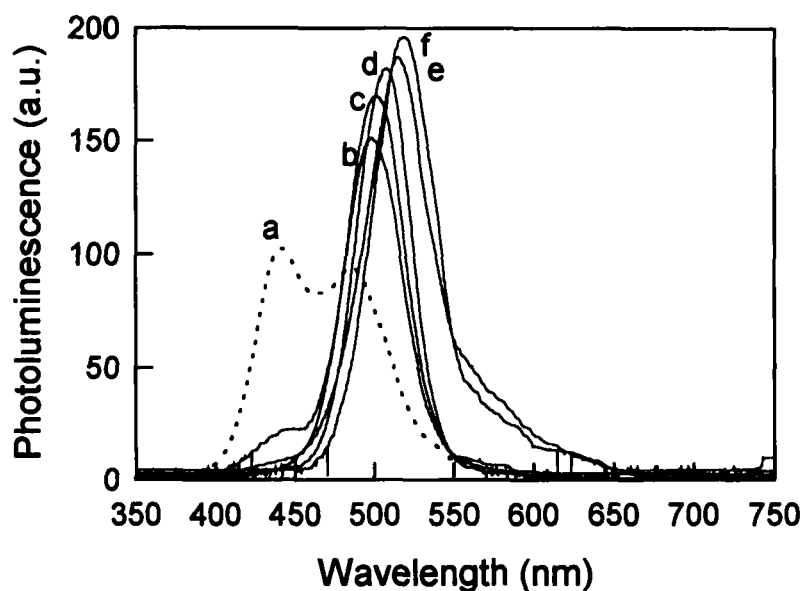


FIGURE 3 Photoluminescence spectra of Alq3/PEI blend films : (a:0/100, b:5/95, c:10/90, d:20/80, e:30/70, f:50/50)

Photoluminescence(PL) of PEI and Alq3/PEI films were shown in Figure 3. PEI shows the double peaks in photoluminescence spectra from ca. 600nm to 400nm. In case of incorporating small amount of Alq3 into PEI matrix, the PL shoulder at 430nm(2.9eV) was appeared due to the presence of PEI. However, this shoulder was disappeared above 10wt.% of Alq3 content. It is considered that the disappearance of this shoulder is due to relatively high luminance of Alq3. With increasing the content of Alq3, the maximum peak of the Alq3/PEI films was moved to lower energy region. This shift of peak maximum is the indirect proof of the existing weak exciplex between

chromophores at 470nm (2.6eV) in PEI and Alq3. It is expected that electroluminescence(EL) spectra are also shifted in the same manner as the PL shift in the Alq3/PEI films (cf. PEI has likely no EL.). The PL of Alq3 was bluish green. From the present results, it is regarded that the color-tuning may be possible if one utilizes the existence of weak exciplex between emitting material and binder polymer.

The structures of Alq3 and Alq3/PEI blend films are shown in Figure 4. Figure 4(a) is the micrograph of Alq3 casted from NMP solution and subsequently softbaked at 90°C. The single crystals like rod and crossed rod type were randomly distributed in the

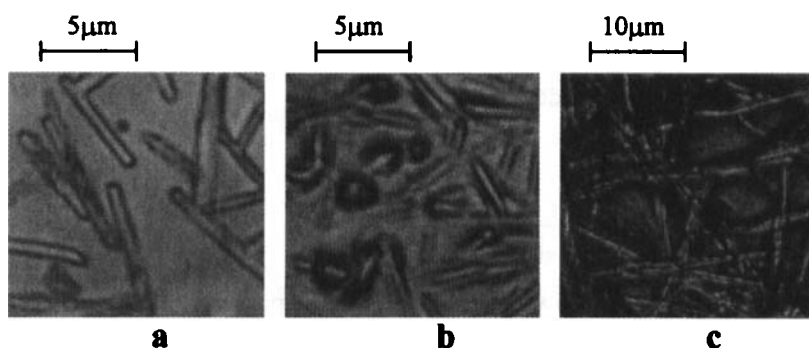


FIGURE 4 Optical micrographs of Alq3/PEI blend films : (a: Alq3, b:30/70, c:50/50) See Color Plate IV.

whole Alq3 film, indicating optically hazy morphology. Clear Alq3/PEI films were obtained at the composition below 20/80 (w/w), while 30/70 composition gave a transition morphology with mixed clear and hazy regions in the same film, and completely opaque film was obtained at 50/50 composition. The film of 30/70 composition shows both of rod-type single crystals and underdeveloped Alq3 particles. In case of 50/50 composition, complicate networks were taken place. Thus one can conclude that the optimum composition of Alq3 and PEI is 20/80 (w/w). It is, however, considered that the hazy films can also illuminate EL but the efficiency may be very low because of worse ohmic contact between metal electrode and films surface, which is quite rough due to phase separation.

CONCLUSIONS

In order to get insights on the electroluminescence properties of the dye-dispersed polymer EL LED, the absorption and photoluminescence spectra of the Alq3-dispersed

PEI films were preliminarily investigated together with film structures. The maximum peak of PEI was shifted to lower energy region in the blend films of Alq3 and PEI, indicating existence of weakly interacted exciplex. On increasing the Alq3 contents, the absorption intensity for Alq3 in the blend films was monotonically increased but no energy shift was observed. However, PL spectra were moved to lower energy state with increasing the content of Alq3, meaning also the existence of an exciplex. It may be assumed that EL may be generated in the EL LED composed of Alq3, PEI, and carrier transporting materials in the similar manner as PL. The films containing above 30wt.% of Alq3 were hazy, showing the morphology of complicate networks. Conclusively, the composition of 20/80 (w/w) is optimum to prepare good Alq3-dispersed PEI EL LED as a thermally stable EL device.

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