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<https://hdl.handle.net/2324/19440>

出版情報 : Applied Physics Letters. 56 (9), pp.799-801, 1990-02-26. American Institute of Physics

バージョン :

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Blue light-emitting organic electroluminescent devices

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(Received 11 September 1989; accepted for publication 18 December 1989)

Organic electroluminescent (EL) devices with multilayered thin-film structures which emitted bright blue light were constructed. Two empirical guides for the selection of blue-emitting materials were established. The keys to obtain the EL cells with high EL efficiency were excellent film-forming capability of an emitter layer and the appropriate combinations of emitter and carrier transport materials for avoiding the formation of exciplexes. In one of our organic electroluminescent devices, blue emission with a luminance of 700 cd/m^2 was achieved at a current density of 100 mA/cm^2 and a dc drive voltage of 10 V.

Organic materials have been expected to be applicable for practical electroluminescent (EL) devices because of their high fluorescence efficiency and semiconducting properties. One of the most fascinating advantages of organic materials is the possibility of a wide selection of emission colors, particularly in the blue region, in EL displays through the molecular design of organic materials. Recently, organic EL devices with bright green and yellow emission which possessed multilayered thin-film structures consisting of an emitter layer and carrier transport layers have been reported.^{1,2} However, the fabrication of bright EL devices with blue emission has not been successful. From the viewpoint of the working principle of organic EL cells, no difficulty specific to blue emission is anticipated. In fact, we have already reported that blue light emission was possible in organic EL devices with an anthracene film as an emitter layer,³ although the blue emission was not bright enough for practical display devices. We expect that the development of new emitter materials surely holds the prospect of bright blue emission.

In this letter, we examined 15 organic materials for blue emission and obtained two empirical guides for their selection. The keys to obtaining EL cells with high EL efficiency were excellent film-forming capability of an emitter layer and the appropriate combinations of emitter and carrier transport materials for avoiding the formation of exciplexes. When we used properly selected emitter and carrier transport materials, high luminance, over 500 cd/m^2 in the blue region, was achieved.

Three types of EL cell structures were used in our study: type A—indium-tin-oxide substrate (ITO)/hole transport layer/emitter layer/MgAg, type B—ITO/emitter layer/electron transport layer/MgAg,⁵ and type C—ITO/hole transport layer/emitter layer/electron transport layer/MgAg.³ The thickness of the organic layers was 500 \AA unless otherwise specified. Organic layers were deposited on a pre-cleaned ITO glass substrate by vacuum deposition, and a cathode MgAg layer was deposited on the organic layer by codeposition. The deposition rate for organic layers was about $2\text{--}4 \text{ \AA/s}$. The emitting area in the cells was $0.2 \times 0.2 \text{ cm}^2$. For a hole transport material, aromatic diamine,⁶ which was known to transport holes selectively, was used. For an electron transport material, we used an oxadiazole derivative (PBD). In a previous letter,⁵ we showed that the

PBD operated as an excellent electron conductor in organic layered structures. In Fig. 1 the molecular structures of two carrier transport materials and organic fluorescent materials⁷ with intense blue fluorescence are listed. All the emitter materials were purified by a train sublimation method⁸ before use. The quality of the emitter films was observed under a microscope with $1000\times$ magnification.

First, 11 organic emitter materials were examined using type A cells. Table I summarizes the emitter materials, the qualities of emitter films deposited on an amorphous diamine film, and photoluminescence (PL) and EL emission wavelengths. The first requirement for achieving high performance in blue EL cells is good quality of the emitter films. Six materials (E1 to E6), which are known as typical organic scintillators, did not give dense thin films. The surfaces of the evaporated films appeared to be rugged; that is to say, the growth of about $1 \text{ }\mu\text{m}$ scale large crystals was observed. The capability of forming smooth layers was closely related to the molecular structure of the emitter materials. In general, organic compounds with blue fluorescence have simple molecular structures with high symmetry and with few substituents. Thus, such molecules possess a tendency to give large crystals, even when they are forced to form thin films. Poor quality of these emitter films resulted in inferior EL cell characteristics, even though we could fabricate several EL cells and observed EL emission from these cells. In contrast, five materials (E7–E11) gave smooth pinhole-free thin films on the amorphous dense layers of a diamine. Evidently, the emission efficiencies of the EL cells with poor quality of the emitter films (E2, E3, E4, E5, and E6) were quite low, and also deviations from a linear relation in luminance-current (L - J) characteristics were observed. On the other hand, the EL cells with smooth, pinhole-free films showed high EL efficiency as shown in the EL cells with the emitters (E7, E8, E10, and E11). One notices that the symmetry of these compounds is rather low and/or bulky substituents are attached in these compounds. Thus, we established a rough criterion for the selection of emitter compounds.

A second requirement concerns the formation of exciplexes between an emitter and a hole transport material (diamine). The emitter materials (E6–E9) were found to form exciplexes with the diamine in solid states, and resulted in a long-wavelength PL emission due to the exciplexes. A typical example of exciplex formation can be demonstrated

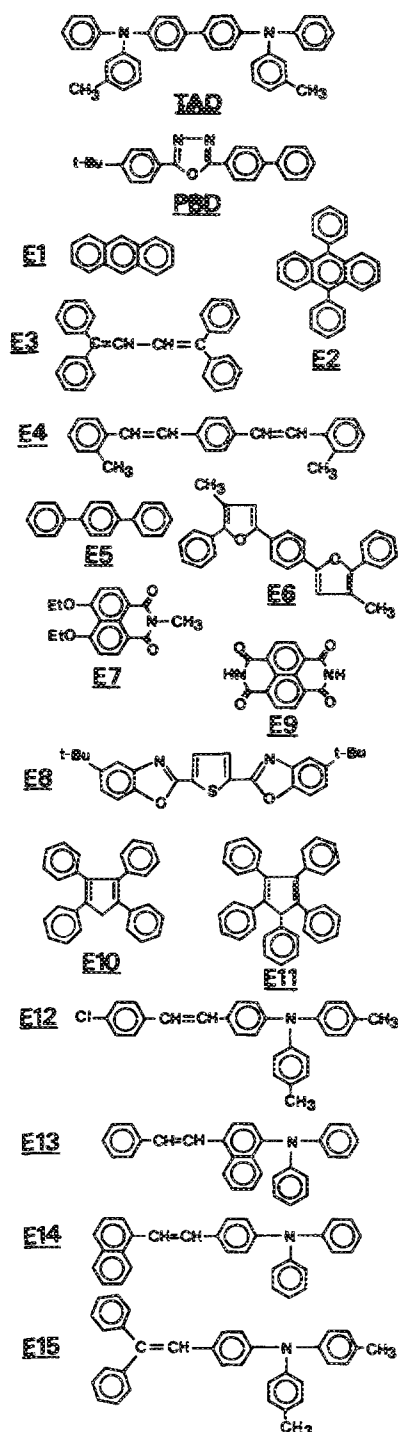


FIG. 1. Molecular structures of two carrier transport and 15 emitter materials.

by the combination of the E8 and diamine (Table I). The evaporated film of a single E8 layer showed its PL at around 435 nm. However, when the E8 and diamine were mixed in solid states, its PL peak shifted to 530 nm. In addition, the EL emission spectrum in this EL cell coincided well with the exciplex emission. Thus, it is suggested that an exciplex was formed at the interface of emitter and diamine layers and also served as carrier recombination and emission sites. Formation of the exciplex at the interface between the two organic layers must be avoided for obtaining blue emission.

TABLE I. Quality of emitter films, PL peaks of emitter films, and EL peaks in type A cells.

Emitter	Quality of film	PL peak (nm) ^a	EL peak (nm) ^b	Luminance (cd/m ²) ^c
E1	fair	420	425	0.02
E2	fair	472	475	0.09
E3	fair	432	430	6
E4	fair	452	460	1
E5	fair	370	...	0.004
E6	fair	478	590 ^d	0.09
E7	good	460	520 ^e	35
E8	good	435	530 ^e	12
E9	good	440	560 ^e	0.08
E10	good	460	460	70
E11	good	467	465	120

^a Peak wavelength of a PL spectrum.

^b Peak wavelength of an EL spectrum.

^c Luminance at a current density of 100 mA/cm².

^d EL intensity was too weak to get the EL peak.

^e Formation of exciplex between an emitter and a diamine.

In the survey of the emitter materials with intense blue emission, we found that phenyl-substituted cyclopentadiene derivatives (E10 and E11) overcame the two difficulties described above. They possess intense fluorescence at ~460 nm in solid states and also form dense and pinhole-free films. The EL cells with these emitters showed good EL performance. The EL cell with the emitter E11 behaved like a rectifier. In a forward bias of the ITO electrode, a large injection current was observed in comparison with a small current of reverse bias. Luminance was linearly proportional to the current in a wide current range, and the luminance of 120 cd/m² was achieved at a current density of 100 mA/cm² and a dc voltage of 13 V. The emission peak was at ~465 nm and coincided well with the PL spectrum of the E11 solid film, indicating no formation of an exciplex.

Success in high EL efficiency was also obtained with type B cells. Table II summarizes the EL characteristics of the fluorescent materials suitable for the type B cell struc-

TABLE II. Quality of emitter films, PL peaks of emitter films, and EL peaks in type B and type C cells.

Type B cells				
Emitter	Quality of film	PL peak (nm) ^a	EL peak (nm) ^b	Luminance (cd/m ²) ^c
E12	good	478	470	360
E13	good	450	460	220
E14	good	469	480	180
E15	good	459	460	400
Type C cell				
Emitter	Quality of film	PL peak (nm) ^a	EL peak (nm) ^b	Luminance (cd/cm ²) ^c
E3	good	432	430	700

^a Peak wavelength of a PL spectrum.

^b Peak wavelength of an EL spectrum.

^c Luminance at a current density of 100 mA/cm².

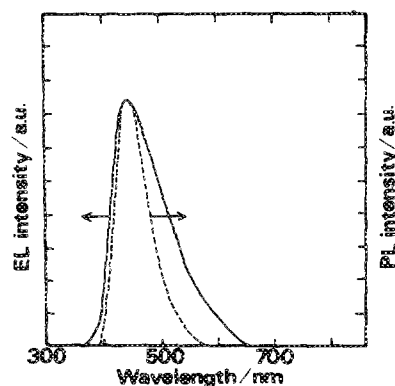


FIG. 2. Photoluminescent and electroluminescent spectra. (solid line) EL spectrum in a ITO/diamine/E3/PBD/MgAg cell, (broken line) PL spectrum of the emitter layer E3.

ture. The empirical guides, mentioned before, are also applicable in this cell structure. These EL cells also exhibited rectification, where the forward bias corresponded to the positive on the ITO electrode. In the case of the cell with E15 as an emitter, a luminance of 400 cd/m^2 at a current density of 100 mA/cm^2 was obtained with a dc voltage of 9 V.

Finally, we discuss our best blue-emitting device. The cell structure was type C with the emitter E3, 350 \AA in thickness. For the emitter material, 1,1,4,4-tetraphenyl-1,3-butadiene, E3, which did not give a pinhole-free thin film in a type A cell, was used. A luminance of 700 cd/m^2 was achieved at a current of 100 mA/cm^2 by applying a dc voltage of 10 V. At this emission intensity, a luminance efficiency of 0.22 lm/W was estimated. The EL efficiency of this cell was about $100\times$ larger than that of the type A cell with the emitter E3. The peak of the EL spectrum was located at 430 nm and coincided well with the PL spectrum of the emitter film, although the full width at half maximum (FWHM) of the EL spectrum was broader than that of the PL spec-

trum (Fig. 2). One of the reasons for high EL efficiency in this three-layer cell is the formation of a stable, dense, and homogeneous emitter layer. The deposition of an electron transport layer on the emitter layer contributed to keeping the morphology of the emitter layer in as-deposited form, drastically retarding the crystallization of the emitter layer. Also, the effect of confinement of carriers and excitons within the emitting layer by the double heterostructure should be considered. We cannot specify, however, which effect is dominant in this cell at this stage.

The stability of the type C cell with the E3 emitter was tested under a constant current density of 10 mA/cm^2 . The initial luminance of 90 cd/m^2 showed a relatively fast decrease (50% in 2 h). At a temperature of 77 K, a constant luminance was retained over 5 h. One of the most likely origins of the degradation of the cells is the crystallization of the organic layers due to produced heat.

In summary, we have obtained the organic EL devices with bright blue emission. Excellent performance of the EL devices can be attributed to the fabrication of pinhole-free films and the exclusion of exciplex formation at the interfaces between the two organic layers. Our empirical guidelines shown in this letter promise further development of blue-emitter materials in multilayered EL devices.

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⁴ITO was purchased from HOYA Co. Ltd., Tokyo, Japan. The thickness of the ITO is 1000 \AA and sheet resistance is $\sim 20 \Omega/\square$.

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⁷The compound (E7) was kindly donated from Mitsubishi-kasei Co. Ltd., Fukuoka, Japan. The compounds (E12-E15) were kindly donated from RICOH Co., Ltd., Shizuoka, Japan. Other compounds were purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin, 53233.

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