Photoluminescence and Electroluminescence Characteristics of 3,3′-Dicyano-[7,7′-biindolizine]-1,1′,2,2′-tetracarboxylic Acid 1,2-Diethyl 1′,2′-Dimethyl Ester

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We investigated photoluminescence (PL) and electroluminescence (EL) characteristics of 3,3′-dicyano-[7,7′-biindolizine]-1,1′,2,2′-tetracarboxylic acid 1,2-diethyl 1′,2′-dimethyl ester (Et_2Me_2-biInd). We found that Et_2Me_2-biInd has efficient blue PL and a multilayer organic light-emitting diode doped with Et_2Me_2-biInd exhibits a relatively high EL efficiency of 1.8 ± 0.1%.

Organic light-emitting diodes (OLEDs) have been intensively developed because of their high potential for use in low-cost, thin, and flexible display and lighting applications.[1,2] However, the performance of blue OLEDs is typically inferior to that of green and red OLEDs. Also, there has been relatively few reports on efficient blue-emitting materials when compared with green- and red-emitting materials. Hence, energetic research on blue-emitting materials having a high photoluminescence (PL) efficiency is very crucial to development of future OLED displays and lighting.

Recently, we found that a wide variety of indolizine and biindolizine derivatives can be easily synthesized and they emit blue PL.[3] Moreover, biindolizine derivatives had much higher PL quantum efficiencies (η_{PL}) than those of indolizine derivatives. The excellent blue-emitting ability and the ease of designing chemical structures of biindolizine derivatives can provide them high potential as a blue-emitting material for OLEDs. Among a series of biindolizine derivatives, we focused our attention on 3,3′-dicyano-[7,7′-biindolizine]-1,1′,2,2′-tetracarboxylic acid 1,2-diethyl 1′,2′-dimethyl ester (Et_2Me_2-biInd) because this material has a high η_{PL} of 82 ± 5% in solution. Although some indolizine and biindolizine derivatives have already been synthesized and reported (see, for example, refs. 4, 5, and 6), PL and electroluminescence (EL) characteristics of Et_2Me_2-biInd have never been reported. In this study, we demonstrated that Et_2Me_2-biInd can be used as a blue-emitting dopant for fabricating blue OLEDs.

The chemical structures of 3-cyanoindolizine-1,2-dicarboxylic acid diethyl ester (Et_2-Ind), 3-cyano-7-phenylindolizine-1,2-dicarboxylic acid diethyl ester (Et_2Ph-Ind), and Et_2Me_2-biInd are shown in Figure 1. The 10^{-5} M solutions of these materials in chlorobenzene were prepared for comparison of their PL characteristics in terms of their chemical structures. The 50 nm layer of wide-energy-gap 4,4′-bis(carbazol-9-yl)-2,2′-biphenyl (CBP) doped with Et_2Me_2-biInd at 3 mol % and the 50 nm pure Et_2Me_2-biInd layer were prepared on cleaned quartz substrates using conventional vacuum deposition. The PL spectra of the samples were measured using a FP-6500 spectrofluorometer (JASCO). The η_{PL} of the solutions was determined using relative PL intensities with a 10^{-5} M *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)$_3$] solution in dichloroethane ($\eta_{PL} = 89 \pm 3\%$) as a standard.[7] The solutions were bubbled with dry nitrogen for 6 h before the measurements. The η_{PL} of the films was also measured using an integrating sphere (C9920, Hamamatsu Photonics). The excitation light wavelength for PL was 350 nm, where the CBP absorption is dominant and the Et_2Me_2-biInd absorption is small in the doped CBP film.

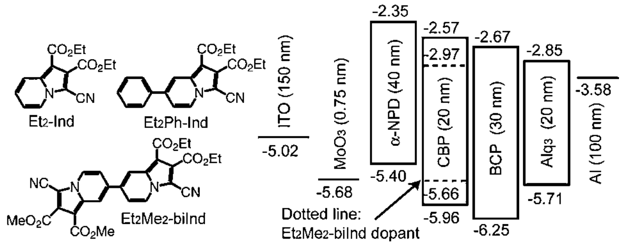

Figure 1. Molecular structures of Et_2-Ind, Et_2Ph-Ind, and Et_2Me_2-biInd and energy level diagram of OLED based on Et_2Me_2-biInd.

The OLED structure was composed of a glass substrate coated with a 150 nm anode layer of indium tin oxide (ITO), a 0.75 nm hole-injection layer of MoO_3,[8,9] a 40 nm hole-transport layer of *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD), a 20 nm emitting layer of 3 mol % Et_2Me_2-biInd-doped CBP or pure Et_2Me_2-biInd, a 30 nm hole-blocking electron-transport layer of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), a 20 nm electron-transport layer of tris(8-hydroxyquinoline)aluminum (Alq_3), a 0.5 nm electron-injection layer of LiF, and a 100-nm cathode layer of Al. The current density–voltage–external quantum efficiency–power conversion efficiency (J–V–η_{ext}–η_{power}) characteristics and the EL spectra of the OLEDs operated at a current of 1 mA/cm^2 were measured at room temperature. The energy level diagram of the OLEDs was obtained using the ionization potential energies and the optical absorption onset energies of the layers (Figure 1). Detailed fabrication and measurement conditions are described in ref. 9.

The PL spectra of the solutions and the films and the EL spectra of the OLEDs are shown in Figure 2. The PL intensities of the derivatives strongly depended on their chemical structures. For example, despite the Et_2-Ind solution showed no PL, the strong blue PL was observed in the other solutions. The η_{PL} was 33 ± 4% for the Et_2Ph-Ind solution and 82 ± 5% for the Et_2Me_2-biInd solution. These results clearly show that the substitution at 7-position of the indolizine framework is crucial for enhancing the PL intensities. We assume that a nonradiative decay process of excited-state molecules is reduced by the substitution at the 7-position using a bulky group. Moreover, the Et_2Me_2-biInd exhibited a relatively large η_{PL} of 67 ± 1% in the doped CBP film and 37 ± 1% for the pure Et_2Me_2-biInd film.

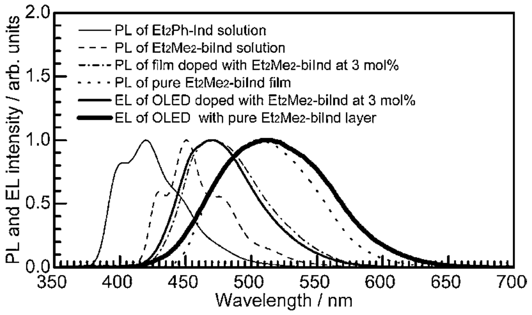

Figure 2. PL spectra of 10^{-5} M solutions of Et_2Ph-Ind and Et_2Me_2-biInd, of film doped with Et_2Me_2-biInd at 3 mol %, and of film of pure Et_2Me_2-biInd and EL spectra of Et_2Me_2-biInd-based OLEDs operated at 1 mA/cm^2.

The shapes of the EL peaks almost corresponded to those of the PL peaks. However the slight difference in peak position between PL and EL was observed, which may be due to a weak microcavity effect.[10] Moreover, we found that the PL and EL spectra gradually shifted to a longer wavelength and the η_{PL} decreased as increasing the Et_2Me_2-biInd concentrations. From these, we conclude that Et_2Me_2-biInd molecules are aggregated in the pure Et_2Me_2-biInd film and concentration quenching of excited-state Et_2Me_2-biInd molecules is suppressed by doping Et_2Me_2-biInd in a wide-energy-gap CBP host to some extent. The PL spectrum of CBP (PL maximum: 392 nm) and the absorption spectrum of Et_2Me_2-biInd (absorption maximum: 392 nm) are well overlapped, suggesting that efficient Förster energy transfer takes place from CBP to Et_2Me_2-biInd. Carrier trapping followed by the carrier recombination on small energy-gap Et_2Me_2-biInd molecules doped in a wide energy-gap CBP host is possible in the case of an EL mode.[11]

The *J*–*V* and *L*–*V* characteristics of the OLEDs are shown in Figure 3a. The driving voltages at a current of 100 mA/cm^2 were 9.6 ± 0.1 V for the undoped OLED and 10.4 ± 0.2 V for the doped OLED. In the undoped OLED, holes are efficiently injected from α-NPD to Et_2Me_2-biInd across a small hole injection barrier of 0.26 eV (see Figure 1). On the other hand, hole injection from α-NPD to Et_2Me_2-biInd and from α-NPD to CBP is less efficient in the doped OLED owing to the small amount of Et_2Me_2-biInd molecules doped in the CBP host and a large hole injection barrier height of 0.56 eV between the α-NPD and the CBP.[12] Thus, the driving voltages of the doped OLED became higher than those of the undoped OLED.

The η_{ext}–*J* and η_{power}–*J* characteristics of the OLEDs are shown in Figure 3b. The maximum η_{ext} and η_{power} were 0.12 ± 0.01% and 0.10 ± 0.01 lm/W for the undoped OLED and 1.8 ± 0.1% and 1.8 ± 0.1 lm/W for the doped OLED. The η_{ext} and η_{power} were markedly improved by doping the Et_2Me_2-biInd in the CBP host layer owing to the suppression of concentration quenching as discussed before. In our separate experiments, we tested OLEDs doped with Et_2Me_2-biInd at various concentrations ranging from 1 to 100 mol %. From results of the OLED characteristics, we found the optimized Et_2Me_2-biInd concentration to be 3 mol %, which provided the highest η_{ext} among the OLEDs with various concentrations.

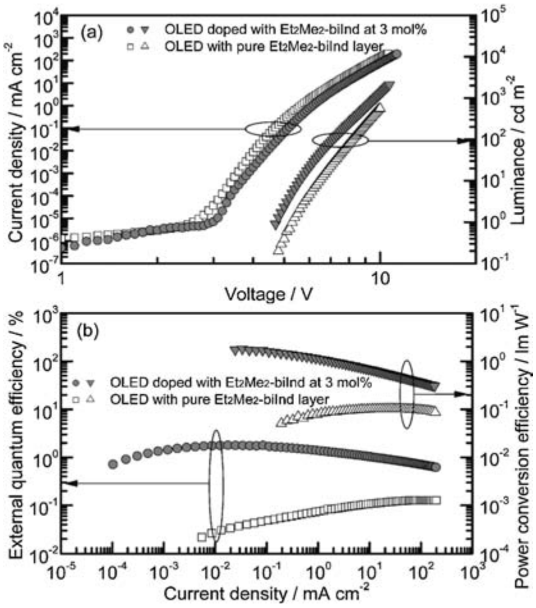

Figure 3. (a) *J*–*V* and *L*–*V* characteristics and (b) η_{ext}–*J* and η_{power}–*J* characteristics of Et_2Me_2-biInd-based OLEDs.

In summary, we have demonstrated that indolizine derivatives can be used as a new class of blue-emitting materials for OLEDs. The dimerization of indolizines at 7-position, Et_2Me_2-biInd, markedly improved η_{PL} when compared with Et_2-Ind and Et_2Ph-Ind. Moreover, concentration quenching of excited-state Et_2Me_2-biInd molecules was suppressed by doping Et_2Me_2-biInd in a wide-energy-gap CBP host. Owing to the PL enhancement, we obtained a relatively high EL efficiency of 1.8 ± 0.1% in an OLED doped with Et_2Me_2-biInd at 3 mol %.

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