Multilayer Organic Electroluminescent Device with Dithienosilole Derivative

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Dithienosilole derivatives (DTS) improved an electron injection efficiency of the typical organic electroluminescent device, indicating that DTS may have a high electron affinity. DTS also exibited a blue light emitting and hole injection properties.

Organic Electroluminescent (EL) devices have potential applications as large-area flat panel displays. In these devices, organic emitter materials are excited by the carrier recombination. Therefore, it is important to balance hole and electron injection to achieve high recombination efficiency. To this end, multilayer device structures having a hole-transporting layer and an electron-transporting layer are often employed. There are a number of papers dealing with hole transporting materials. [1-7] On the other hand, electron-transporting materials are limited and the development of new materials with higher electron-transporting property are expected. [8-10] Recently, silole derivatives having low-lying LUMO levels have been reported to be useful as electron-transporting materials in EL devices. [11] In this paper, we synthesized novel dithienosilole derivative (DTS), which may have lower LUMO level than those reported earlier, [12-14] and investigated the EL properties (Figure 1).

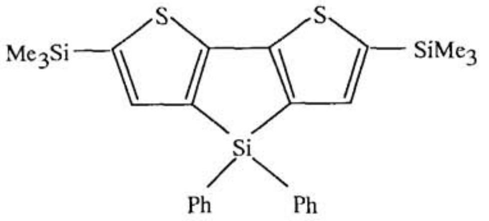

Figure 1. Chemical structure of dihienosilole derivatives.

For the evaluation of DTS, we fabricated, by vacuum deposition, four kinds of multilayer devices. In addition to the dithienosilole derivatives, we used N,N'-diphenyl-N,N'-bis (3-methylphenyl) - 1, 1' - biphenyl - 4,4' - diamine (TPD) and an tris(8-quinolinolato) aluminum (Alq) electron as a hole-transporting material and an electron-transporting material, respectively. The device structures and the thickness of each layers are as follows:

Type I: ITO/ TPD (40 nm) / Alq (50 nm) / DTS (10 - 20 nm) / Mg:Ag
Type II: ITO / TPD (30 nm) / DTS (50 nm) / Alq (20 nm) / Mg:Ag
Type III: ITO / DTS (10 - 20 nm) / TPD (30 nm) / Alq (60 nm) / Mg:Ag.

For comparison, a typical two layer device, ITO/ TPD (40 nm) / Alq (60 nm) / Mg:Ag, was also fabricated as type IV. The morphology of the DTS film is almost equal to that of the TPD and Alq from the measurements of the surface of the DTS with a Sloan Dektak 3030 surface profiler.

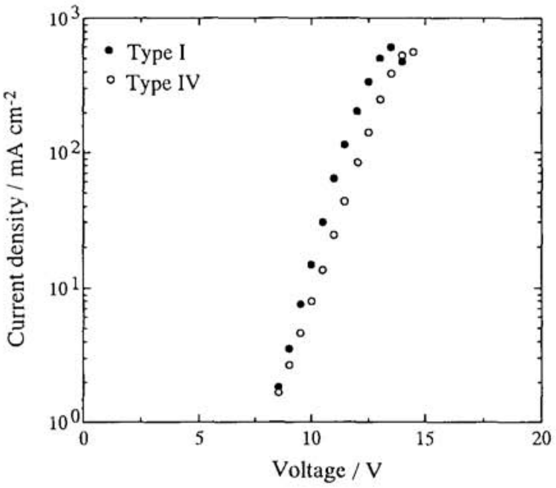

Figure 2. The comparison in the elecrical properties of EL devices with dithienosilole (Type I) as an electron injection layer and without (Type IV).

From the type I device, green electroluminescence was observed and the EL spectrum were almost identical to the photoluminescence (PL) spectrum of vacuum deposited film of Alq, implying that the EL originated from the Alq layer. Figure 2 shows the current density-voltage characteristics of the devices type I and IV. The current density of the type I device is higher than that of type IV at the same operating voltages. Since the hole transporting material for both device is the same, TPD, the difference in I-V curve should arise from the electron transport layer. It is known that the device operating voltage depends partly on the barrier height for carrier injection at the electrode interfaces. It is reasonable to assume that the barrier height for electron injection for the type I device is lower than that of type IV device, which results in the lower voltage required for the electron injection for the type I. The pseudo LUMO level of DTS caluculated from both ionization potential and electronic absorption spectrum was comparable to that of Alq (3.1 eV), indicating that the DTS has high electron affinity same as the Alq. The measurements of ionization potential were carried out using Riken AC-1. Figure 3 shows the luminance (L) -voltage (V) characteristics of the type I device. For comparison, the L-V characteristics for the type IV device is also plotted. The L- V characteristics of the type I device were almost comparable to

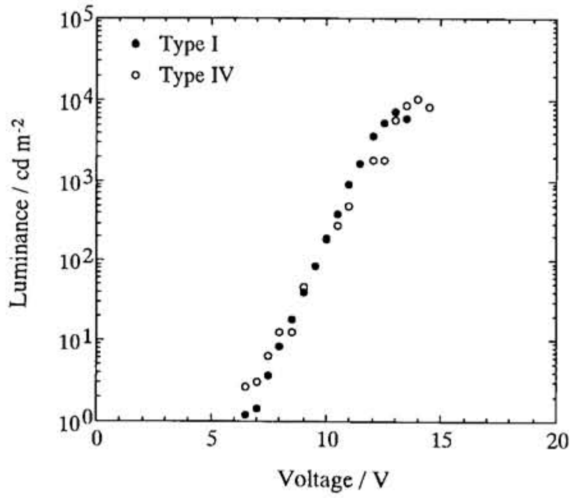

Figure 3. Luminance-voltage characteristics of EL device type I and IV.

those of the type IV device although the luminance level of the type I device is slightly higher at 10 to 12 V than that of the type IV. The higher luminance for the type I at 10 to 12 V is attributed to the higher current density. The reason why the luminance of the type I is almost same as that of the type IV may be that the DTS with the low melting point (158-160 °C) was changed by the heat of the EL device occured or a luminance efficiency of Alq decreased due to the diffusion of the DTS to the Alq layer.

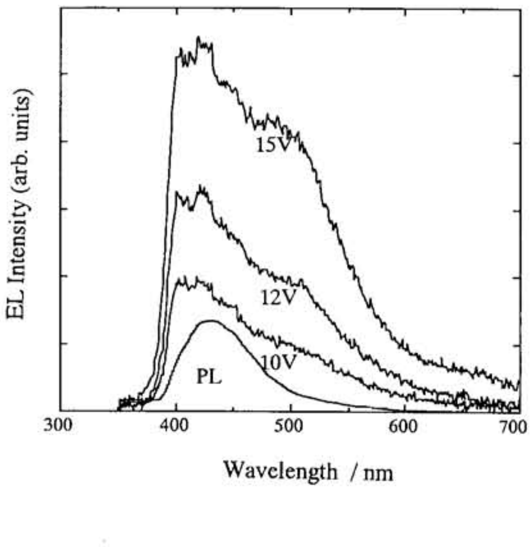

Figure 4. EL spectrum under several voltage on device type II and PL spectra of solid film (DTS).

The DTS was also examined as an emitter material in the device type II. From this device, blue electroluminescence was observed as shown in Figure 4. As increasing the applied voltage the EL color changed from blue to whity blue. A maximum luminance of 1200 cd/m^2 is achieved at 16 V. Comparing with the PL spectrum of the vacuum deposited film of the DTS , the EL originates not only from the DTS layer but also from the Alq and TPD layer, which indicates that the carrier recombination takes place at the DTS layer as well as the Alq and TPD layer. The two peaks of 400 and 410 nm are caused from the TPD and the shoulder peak of 410 - 420 nm from the DTS. This further implies that DTS has a bipolar carrier transport property. When the DTS is used as a hole transport layer in the device type III, I-V and L-V characteristics are comparable to those of the device type IV. This supports our assumption of the bipolar carrier transport properties of DTS. The ionization potential (6.1 eV) of DTS was larger than that (5.2 eV) of TPD, implying that the the hole injection efficiency from the ITO to the DTS may be lower than that from the ITO to the TPD. From these measurements of the ionization potential we can not explain simply the hole injection propeties of the DTS same as that of the TPD. The hole injection properties of the DTS may depend strongly on other properties as the situation of the contact between DTS and ITO.

In conclusion, we synthesized a novel dithienosilole derivative (DTS) and demonstrated that DTS is blue emitter having bipolar carrier transporting property. Further study on carrier injection mechanism of DTS is undertaken and the results will be published elsewhere.

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13 Data for dithienosilole derivatives : mp 158-160 °C; MS m/z 490 (M$^+$); ^{1}H NMR δ ($CDCl_3$) 0.33 (s, 18H, Me_3Si), 7.24 (s, 2H, thiophene ring protons), 7.28-7.42 (m, 6H, Ph), 7.64 (dd, 4H, J=8.1, 1.5 Hz, *o*-Ph protons); ^{13}C NMR δ ($CDCl_3$) 0.1, 128.1, 130.2, 132.3, 135.5, 136.5, 141.7, 142.2, 155.6. Anal. Found: C, 63.43; H, 6.08%. Calcd for $C_{26}H_{30}S_2Si_3$: C, 63.62; H, 6.16%.

14 Ab initio calculations were carried out by using Gaussian 94 program at the RHF/ 6-31G level of theory. The LUMO levels of silole and dithienosilole are 2.52 eV and 1.75 eV respectively.