

Notes

Synthesis and Emission Characteristics of Novel Red Electroluminescent Dye Containing CN Group

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Recently lots of attentions have been concentrated on organic electroluminescent (EL) displays. Various kinds of organic materials such as vacuum-sublimed dye films and fully π -conjugated polymers, polymers with chromophores on skeletal chains or side-chains and polymers-dispersed dye films can be estimated for organic EL devices.¹⁻⁹ Today many researches have been actively conducted to develop a full-color display. However one of serious problems for developing commercial full color goods is instability of organic materials in the EL devices, so several kinds of methods were adopted to increase a long-term stability of the EL device.^{10,11} One approach is to use high performance materials having high emission efficiency and thermal and electrochemical stability for EL devices.

These studies are focused on developing novel dye structures with high durability and high emission efficiencies. In our previous report,¹² D-BCN material composed as a molecular structure with CN groups exhibited bipolar characteristics as well as high emission efficiencies even in single-layer devices. Based on the design concept for charge injection and transport and emissive materials, novel EL

material, D-CN system was studied. Through changing substituted positions of CN groups of D-BCN molecular structure, π -conjugation length between the donor and acceptor groups of D-CN material is shorter than that of D-BCN material so that D-CN material will show different photonic and electronic characteristics. D-CN material also reveals bipolar characteristics due to two kinds of substitution groups, the amine and cyano groups. The molecular structures of D-BCN and D-CN were shown in Figure 1.

Experimental Section

Materials. Synthetic method of novel fluorescent dye, D-CN was shown in Figure 2. The first step is well known as Ullmann reaction and the second step is Vilsmeier-Haack reaction, which referred to the previous paper.⁷ The fluorescent product, D-CN was synthesized by Knoevenagel reaction method as the following step. 4-aldehyde 4'-methoxy triphenylamine, **1** (1.09 g, 2.73 mmol) and 1,4-phenylenediacetonitrile, (0.17 g, 1.09 mmol) were added to the mixture solution of chloroform (9 mL) and ethanol (3 mL). After the addition, sodium methoxide (1.02 g in 28% methanol solu-

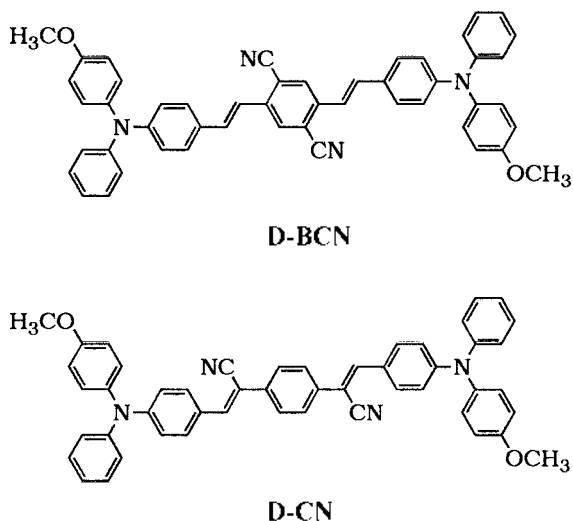


Figure 1. Molecular structures of D-BCN and D-CN.

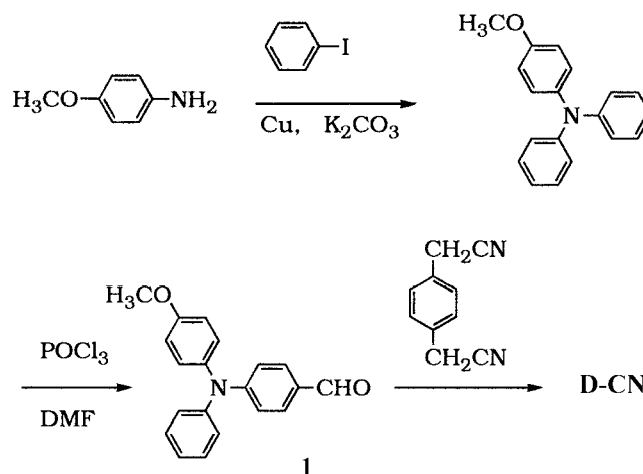


Figure 2. Synthetic routes of D-CN.

tion) was added to the reaction solution. Reaction solution was stirred for 24 hours at the room temperature. After the reaction ended, chloroform (100 mL) and H₂O (100 mL) were poured and the organic layer was selected and dried. The residue was purified by column chromatography (ethyl acetate: *n*-hexane = 1 : 3) and 0.26 g of D-CN was obtained as 32% yield.

¹H NMR (CDCl₃) δ 3.82 (s, 6H, -O-CH₃) 7.79-6.73 (m, 32 H, aromatic H and vinylic H); ¹³C NMR (CDCl₃) 55.50, 106.08, 115.05, 118.65, 119.44, 124.11, 125.15, 125.42, 126.01, 128.17, 129.48, 130.85, 135.10, 139.23, 141.85, 146.54, 150.50, 157.17; IR (KBr) 2190 cm⁻¹ (C-CN, -CN stretching), 980 cm⁻¹ (-C=C-H, trans C-H bending); Anal. Calcd. for: C, 82.62; H 5.27; N, 7.71. Found: C, 81.68; H 5.42; N 7.41.

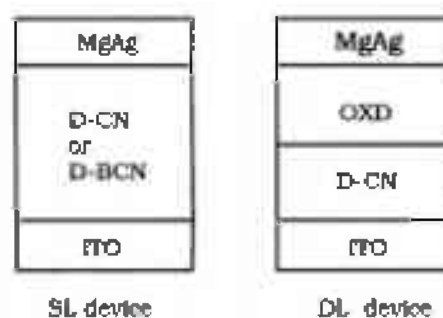
Device fabrication and measurement. Organic layers and metal electrode were formed by conventional vacuum-vapor deposition onto the indium tin oxide (ITO) coated glass substrate from tantalum boats and metal sources under a vacuum of 10⁻⁴ Pa. The thickness of an organic emission layer was 100 nm in a single-layer (SL) device, however in a double-layer (DL) device, oxadiazole derivative (OXD) layer with 30 nm thickness was also deposited onto the organic emission layer. On the top surface of the organic layers, MgAg (weight ratio 9 : 1) mixed film as a cathode electrode was formed as the 200 nm thickness.

The measurements of brightness were conducted using a photon counter (Hamamatsu Photonics, C767). Relative EL intensity values were changed into luminance values using a luminance meter (Topcom BM-8). EL spectra were obtained through a 100 mm monochromator and a photon counter. The photoluminescence (PL) spectrum was obtained using a fluorospectrometer (Hitachi 650/60).

Results and Discussion

Novel EL material, D-CN was designed and made through the synthetic route, Figure 1 and analyzed through ¹H-NMR, ¹³C-NMR, IR and Atomic analysis. Through these analyses it was confirmed that the designed molecular structure was obtained.

Two kinds of devices named as the SL device and the DL device were fabricated for the emission characteristics of the organic material. The structure of SL device was composed of ITO/D-CN or D-BCN as an emission layer/MgAg and in the case of DL device the device structure was ITO/D-CN/OXD/MgAg. Here the OXD layer was used as an electron transport layer. Figure 3 showed the device structures and molecular structure of OXD. Current density and luminance relationships between two different kinds of EL devices with D-CN layer as an emissive layer were represented in Figure 4. In the SL device with D-CN layer, luminance of about 1440 cd/m² was achieved at the current density of 100 mA/cm² and the maximum luminance was detected as 5080 cd/m² in 750 mA/cm². In the case of DL device with D-CN layer, luminance of 3290 cd/m² reveals in the current density of 100 mA/cm². In comparison of two kinds of devices,



Structures of three types of EL devices

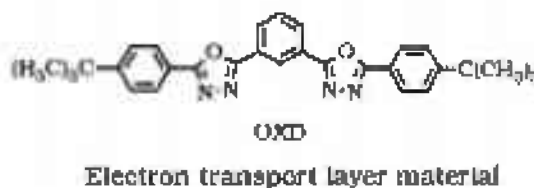


Figure 3. Structures of EL devices and molecular structure of OXD.

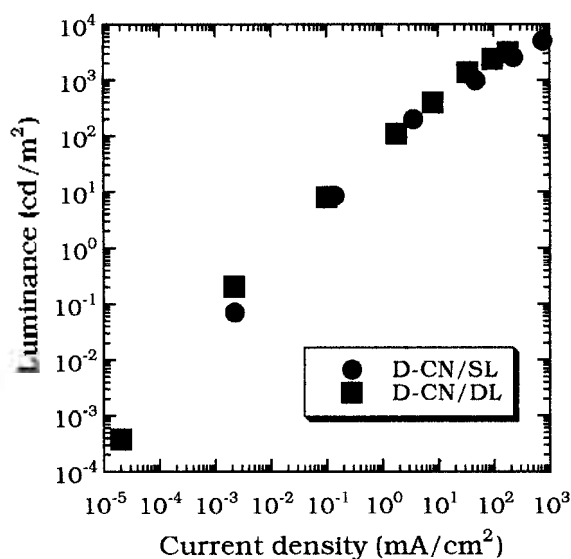


Figure 4. Luminance-current density characteristics of SL and DL devices with a D-CN layer as an emissive layer.

luminance of the SL device showed a little difference in comparison of that of the DL device at the same current densities. These results meant that D-CN material showed bipolar characteristics which was predicted from the molecular structure of D-CN with both two CN groups as the electron injection and transport parts and two amine groups for the hole injection and transport capabilities. Figure 5 shows external quantum efficiency and current density relationships of the SL and DL devices with D-CN or D-BCN layer. When quantum efficiency of the SL and DL devices with D-CN layer were evaluated at the current density of 100 mA/cm², the SL device was estimated as 1% efficiency and the DL device was 1.1% efficiency, which represented about quarter values of the maximum external quantum efficiency

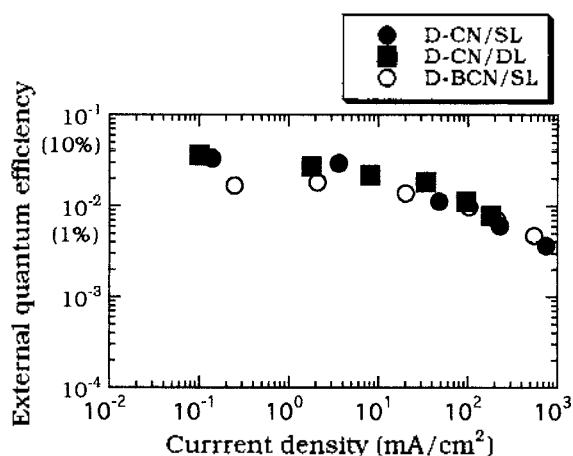


Figure 5. External quantum efficiency and current density relationships of various EL devices.

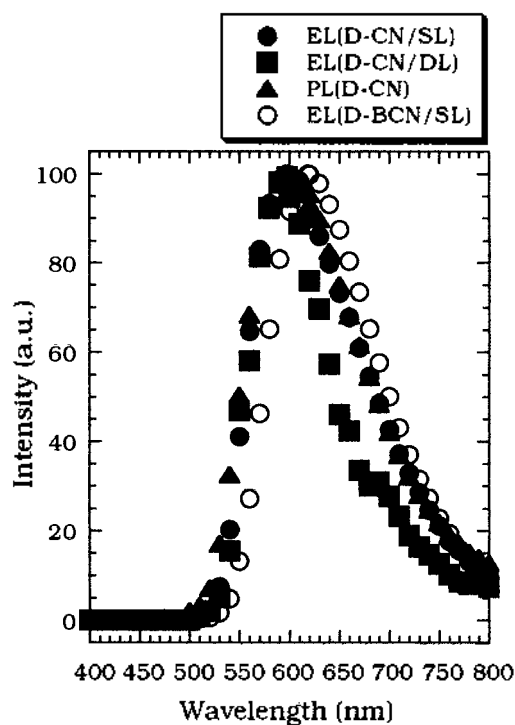


Figure 6. EL spectra of various EL devices, and PL spectrum of a D-CN film.

calculated in EL devices. In comparison of two kinds of material, D-CN and D-BCN in the SL devices, quantum efficiencies are almost the same as about 1% respectively. Therefore both D-CN material and D-BCN material are estimated as the excellent EL emission materials with charge injection and transport capabilities. The PL spectrum of D-CN thin film and EL spectra in the three types of EL devices were showed in Figure 6. In the D-CN material, the EL spectrum of the SL device was measured at 597 nm with the maximum intensity and in the DL device the maximum peak

was detected at 598 nm. The two kinds of luminances in the EL devices with D-CN material revealed almost the same peak curves with red emission color, however a EL spectrum of SL device with D-BCN material shows the maximum intensity of about 630 nm, which is about 30 nm red shift from EL spectra shown in D-CN material. These difference between D-CN and D-BCN is owing to the amount of π -conjugation length with the donor and acceptor interactions. Additionally two EL spectra of D-CN material are coherent with PL of D-CN film, which clearly explains that the emission occurred at only the designed emission layer without unexpected emissions due to an eximer or exiplex within or between device layers.

In conclusion new EL material, D-CN was successfully synthesized and showed excellent EL efficiencies and bright red luminance even in the SL device. Thus D-CN dye can be estimated as an emission material with bipolar characteristics in the EL devices. In the future two kinds of devices, the SL device and the DL device using D-CN material as an emission layer will be estimated about long term working stability. Also various kinds of D-CN derivatives will be synthesized and evaluated in EL devices.

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