

New green fluorescent materials for OLEDs

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Abstract

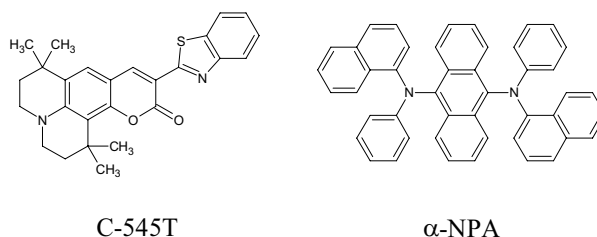
We developed new green emitting materials based on the spiro moieties. The introduction of a spiro linkage into the structure of DJGH series lead to a reduction in crystallization tendency and an increase in glass transition temperature. they showed much better emitting efficiency and color purity than commercial host material Alq₃.

1. Introduction

Numerous conjugated organic molecules have been synthesized and reported to exhibit electroluminescence, from red to green and blue¹⁻³. Although considerable research efforts in Organic Light Emitting Diodes (OLEDs) field have been carried out to enhance the performance suitable for practical use, a lot of problems, e.g., life time and EL efficiency, color purity have still remained. Generally, to improve life time of OLED device, the organic materials which have a high glass transition temperature (T_g) could be used. One effective way to raise T_g is to introduce spiro moiety in organic materials. Spiro type molecules can afford various functionalities, e.g., improvement of solubility, increase of charge carrier mobility, tunable electronic structure, and aggregate suppression to improve morphological stability⁴⁻⁷.

In this study, we developed new green fluorescent materials base on spiro moiety for high performance OLED device

aluminum(Alq₃, TCI) and 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-[1]benzopyrano-[6,7,8-ij]quinolizin-11-one (C-545T, TCI, scheme 1) were used as purchased. The dopant material 2-methyl-9,10-di(2-naphthyl)anthracene (α -NPA, scheme 1) were prepared by methods previously reported⁸. All chemicals used for electroluminescent devices were further purified by vacuum sublimation. UV-vis spectra were recorded on a Shimadzu, UV-1601PC model while photoluminescence (PL) spectra were taken using a Jasco FP-6500 fluorescence spectrophotometer. The glass transition temperatures of compounds were determined by differential scanning calorimetry (DSC) under a nitrogen atmosphere using a Perkin-Elmer DSC 7 instrument at a heating rate of 10 °C/min. The thermochemical stability of DJGH series were measured thermogravimetric analysis (TGA) under a nitrogen atmosphere using a Shimadzu TGA 50 thermal analyzer at a heating rate of 10 °C/min. Photoelectron spectra were obtained on a Riken Keiki photoelectronic AC-2 spectrometer.



Scheme 1. Doping materials

2. Experimental

General Information. *N,N'*-Di-1-naphthyl-*N,N'*-diphenylbenzidine(NPB, TCI), Tris(8-quinolinolato)

OLED Fabrication and Measurement. Indium tin oxide (ITO) with a sheet resistance of 12 Ω /square on clean glass was patterned as an active area of 4 mm²

(2 mm × 2 mm). Prior to device fabrication, the ITO substrates were cleaned by sonication in deionized water, boiled in IPA for 20 min, and dried with nitrogen. Finally, the substrates were dry cleaned using plasma treatment in an O₂ and Ar environment. Organic layers were deposited sequentially by thermal evaporation from resistively heated alumina crucibles onto the substrate at a rate of 1.0 Å/s. The thicknesses of DJ-HIL1 (HIL), NPB (HTL), DJPH-N:X% dopant;C-545T or α -NPA (EML) and Alq₃ (ETL) layer were about 600, 300, 400 and 200 Å, respectively. Before the deposition of metal cathode, LiF was deposited onto the organic layers with the thickness of 10 Å. A high-purity aluminum cathode was deposited at a rate of 5.0 Å/s with the thickness of 2000 Å as the top layer. After the evaporation chamber was vented with nitrogen gas, the device was immediately transferred to a glove-box upon fabrication. A thin bead of epoxy adhesive was applied from a syringe around the edge of a clean cover glass. To complete the package, a clean cover glass was placed on the top of the device. The epoxy resin was cured under intense UV radiation for 3 min.

The current-voltage characteristics of the encapsulated devices were measured on a programmable electrometer having current and voltage sources, Source Measure Unit, model Keithley 237. The luminance and Electroluminescence spectra were measured with a PR650 system (Photo Research Co. Ltd.).

3. Results and discussion

We obtained three products of DJGH-P, DJGH-N, and DJGH-B containing a spiro skeleton for green host materials. The thermal properties of the spiro-linked derivatives were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed in the temperature range from 20 to 400 °C. Figure 1 displays first scanned DSC curves of melting point of DJGH-P, DJGH-N, and DJGH-B at 302, 347, 367 °C respectively. When the amorphous glassy samples is heated again, a glass transition occurs at 157, 179, 173 °C. This observation indicates the prominent stability of these materials, which can be attributed to the presence of the spiro linkage.

DJGH-B exhibit high thermochemical stability, as evidenced by thermogravimetric analysis, with its 5% weight loss temperatures under nitrogen atmosphere being up to 450 °C.

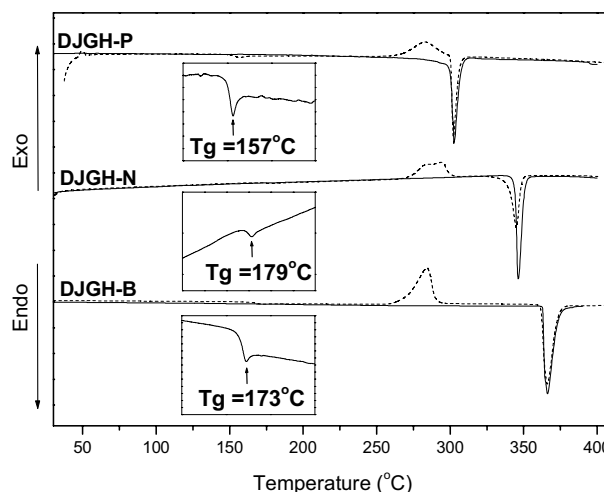


Figure 1. DSC thermograms of DJGH series (—)1st scan and (---)2nd scan

The maximum absorbance of DJGH-P, DJGH-N, and DJGH-B appeared at around 444, 445, and 445 nm in chloroform. Three compounds also showed similar PL spectra in the green region at 469, 475 and 473 nm, respectively (Figure 2).

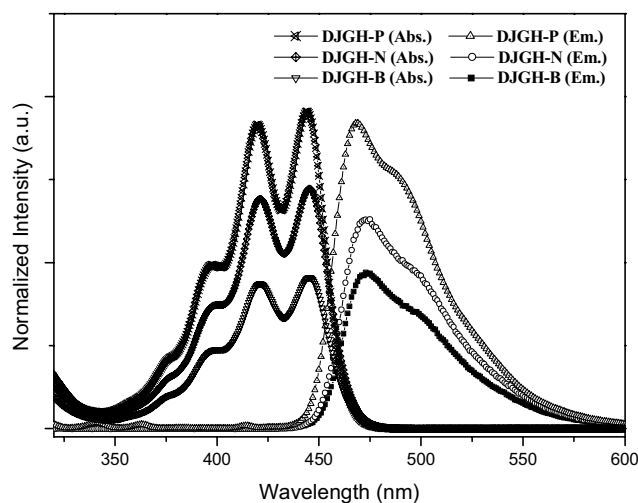


Figure 2. UV-Vis absorption and photoluminescence spectra of DJGH series.

The HOMO was determined using a photoelectron spectrometer, while LUMO was calculated based on the HOMO energy level and the lowest-energy absorption edge of the UV-vis absorption spectrum⁹. The HOMO energy of DJGH-P, DJGH-N, and DJGH-B are at ca. 5.8, 5.7 and 5.7 eV, respectively. LUMO

energy was calculated 3.0 eV in all compounds.

To study the electroluminescence properties of DJGH-N, we fabricated multilayer devices with the configuration of ITO/DJ-HIL1/NPB/DJGH-N:C-545T/Alq₃/LiF/Al. The DJGH-N doped with C-545T emissive layer was produced by co-depositing DJGH-N and C-545T. The EL emission spectra of the OLEDs obtained from undoped and 0.2%, 0.5%, 1.0%, 2.0% of C-545T doped DJGH-N as the emitting layer at 5 V (Figure 3).

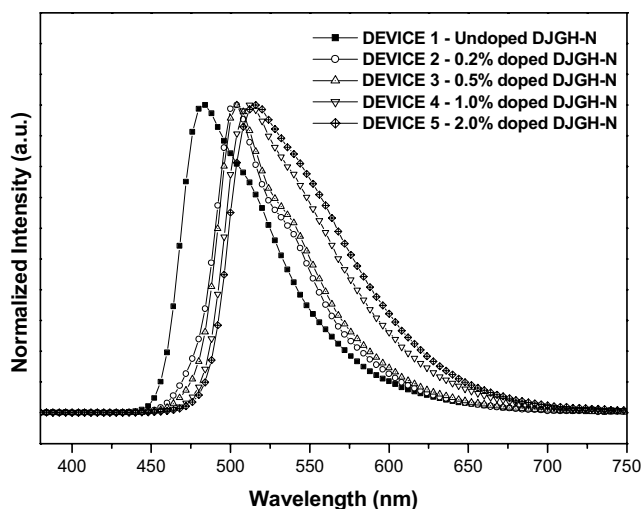


Figure 3. EL spectra of DJGH-N doped C-545T

EL maximum values of Device 1~5 showed at 484 and 504, 504, 512, 516 nm, respectively. At a dopant concentration of 0.2 %, the EL spectrum shows C-545T emission together with a contribution from the host emission of DJGH-N that is due to their incomplete energy transfer. Increasing the doping level to 1.0% results in a maximum energy transfer.

Table 1 presents the EL data of X% C-545T doped DJGH-N for emissive layer at 5V. As rising the C-545T concentration to 2%, the efficiency increases to 8.03 cd/A, with a red-shift in the CIE coordinate(x=0.34, y=0.60). We noted that the EL efficiency drops on going from a dopant concentration of 1.0 to 2.0%. This may be due to self-quenching of the dopant emission at higher concentration

Diaminoanthracene derivative have been used as green emitting materials^{8,10}. UV-vis absorption and photoluminescence maximum wavelength of α -NPA was reported 456 nm and 524 nm (in CH₂Cl₂). Also, the HOMO and LUMO energy level of this product are at ca. 5.54 and 3.11 eV, respectively. We expect

that the efficient energy transfer from host materials to dopant occurs in the emissive layer because of high degree of overlap area in absorption of dopant and emission of DJGH series. DJGH series are also nonpolar molecules which are composed of carbon and hydrogen. When it used green dopant of nonpolar type which is suitable for the DJGH series, we can be expected high efficiency for green emitting device.

Table 1. EL data of DJGH-N:C-545T used emissive layer at 5 V.

Doping Conc.	0%	0.2%	0.5%	1.0%	2.0%
Luminance (cd/m ²)	268	662	626	721	857
C.D (mA/cm ²)	6.28	12.2	9.26	8.47	10.7
L.E (cd/A)	4.27	5.43	6.76	8.51	8.03
P.E (lm/W)	2.68	3.41	4.25	5.35	5.05
C.I.E (x, y)	0.20 0.44	0.25 0.59	0.26 0.60	0.31 0.60	0.34 0.60

We fabricated with α -NPA as doping material for DJGH-P, DJGH-N, DJGH-B and Alq₃ green host materials, respectively. The EL emission spectra of the devices 6~9 containing 5% α -NPA at 7 V can be seen in Figure 4.

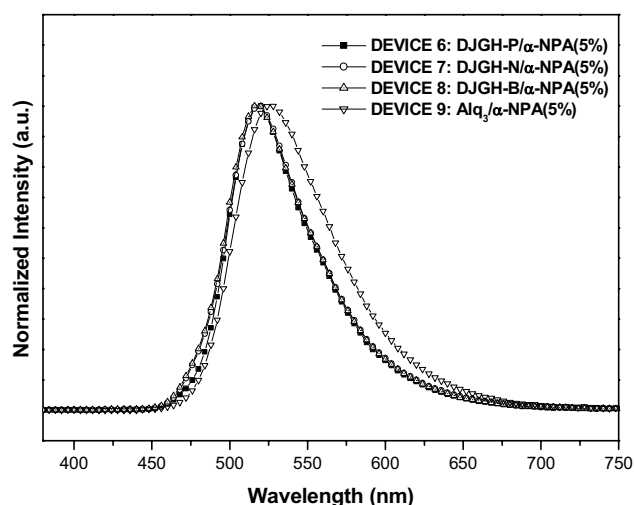


Figure 4. EL spectra of DJGH series and Alq₃ doped α -NPA

The emission maximums of these device fall in the

range 512~528 nm with device 9(Alq₃/5% α -NPA) giving the longest emission peak 528 nm. The EL spectra of device 6~8 closely resembles the PL spectrum of α -NPA⁸ caused by their complete energy transfer from the host and dopant materials. Also, device 6, 7 and 9 are very similar in bandwidth (FWHM = 64 nm), wavelength, and thus the CIE values. The CIE coordinates of the four devices made of DJGH-P, DJGH-N, DJGH-B and Alq₃ were (x=0.28, y=0.62), (x=0.28, y=0.61), (x=0.27, y=0.61) and (x=0.32, y=0.61), respectively (Table 2). Although device 9 also reveals a maximum emission at the wavelength close to the value of device 6~8, its EL spectrum have much boarder FWHM, 74 nm.

Table 2 present key EL data of DJGH series and Alq₃ doped α -NPA for emissive layer. The Luminance of device 8 (DJGH-B/5% α -NPA) at 7 volt were 1389 cd/m², improved by ca. 100% compared to this of device 9. The use of DJGH-B as green host material brings further improvement in the performance of the devices.

Table 2. EL data of DJGH series; α -NPA used emissive layer at 7 V.

Green Host	DJGH-P	DJGH-N	DJGH-B	Alq ₃
Brightness (cd/m ²)	833	630	1389	673
C.D (mA/cm ²)	8.68	8.60	15.4	10.2
L.E (cd/A)	9.59	7.33	9.00	6.62
P.E (lm/W)	4.30	3.29	4.04	2.97
C.I.E (x, y)	0.28 0.62	0.28 0.61	0.27 0.61	0.32 0.61

4. Summary

We have demonstrated that new fluorescent materials containing spiro linkage are green host materials. These materials exhibit excellent physical properties such as remarkable thermal stability and high melting points and glass transition temperatures. DJGH series are good energy transfer to dopant in emitting layer of electroluminescent device. The devices made using DJGH series doped C-545T and α -NPA showed emission with a maximum EL

emission at around 504 and 528 nm. The EL device with a DJGH-B and α -NPA doping concentration of 5% exhibited efficient green light emission at 520 nm and a luminance of 1389 Cd/m² at a current density of 15.4 mA/cm². Its maximum efficiency is 9.0 cd/A (4.04 lm/W) and its CIE coordinates are x=0.27, y=0.61. When DJGH series were adopted for suitable dopant material such as α -NPA, they showed much better emitting efficiency and color purity than commercial host material Alq₃.

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5. References

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