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Color Tuning of Novel Indenopyrazine Core Emitter System by Using Side Group Effect

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A new core material, indenopyrazine, was substituted with diphenylamine groups on the locations 2 and 8, to synthesize new green emitting material, DPA-SPY, for OLED, of which emission wavelength was changed by adjusting the dipole property and the conjugation length. And, DPA-SPY was used as an emitting material layer when non-doped devices were fabricated, and the features were checked: DPA-SPY showed a sharp green spectrum, as with the EL maximum wavelength of 500 nm, narrow FWHM of 49 nm, CIE coordinates of (0.288, 0.538), and luminous efficiency of 0.99 cd/A at the current density of 10 mA/cm^2.

Keywords Color tuning; green emitting material; indenopyrazine; luminescence; OLED

Introduction

Studies on functional organic materials have recently increased in a lot of fields, and especially the field of optoelectronics is exhibiting remarkable results [1]. It is one of present issues that such organic materials consist of core and side groups in terms of chemical structure. So the effects of changes in core and side groups on the properties of the materials have been reported [2].

Organic Light-Emitting Diodes (OLEDs), which is attracting increasing attention in the field of optoelectronics, are based on organic molecules and can realize full-color display applications. There have been thus many studies on them [1,2(c)]. The materials having been reported so far are red, green and blue emitters, and they require high EL efficiencies, good thermal properties, long lifetimes and pure color coordinates (Commission Internationale de l'Eclairage (CIE)) [4].

The function of organic light emitting materials is generally determined by three factors: color purity, efficiency and device life-time. In case suggesting a new synthesized organic light emitting material, it is synthesized by centering on the aspect of

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Address correspondence to Prof. Jongwook Park, Department of Chemistry/Display Research Center, The Catholic University of Korea, 43-1, Yeokgok, Wonmi, Bucheon 420-743, Korea (ROK). Tel.: (+82)2-2164-4821; Fax: (+82)2-2164-4764; E-mail: hahapark@catholic.ac.kr color. It can be the conjugation length inside molecules, the dipole intensity of molecules and the molecular interaction arising by molecular packing which decide the color of organic light emitting materials.

In our previous study, we have reported for the first time novel core organic materials, indenopyrazine derivatives, and by using them, developed new highly efficient deep-blue emitters with high external quantum efficiency of 4.6%, EL spectrum of 450 nm, CIE coordinates of (0.154, 0.078) and FWHM of 47 nm [5]. These days, organic light emitting diodes (OLEDs) are being actively researched and applied to wide full-color displays, thanks to the high efficiency and color purity. It is essential to develop primary color (red, green, blue) materials for full color displays. This study thus changed the side group of indenopyrazine, a new core of organic light emitting materials, to control the band-gap for the purpose of improving the function of green emitting materials. As indenopyrazine includes in the core-structure, imine groups which have sp^2 properties, it tends to slightly pull electrons. Therefore, diphenylamine being capable of pushing electrons was applied to indenopyrazine groups pulling electrons, to have bipolarity in molecules and the emission wavelength of indenopyrazine, as a good chromophore, was adjusted by enhancing the conjugation effect [6].

Experimental

General Method

^{1}H-NMR spectra were recorded on Brucker, Advance 500 and fast atom bombardment (FAB) mass spectra were recorded by JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained by the HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo- and electro-luminescence spectroscopy. The redox potential of synthesized materials was measured at the scanning rate of 100 mV/s by WBCS 3000 system, a cyclic voltammeter, and acetonitrile (AN) containing 1 M tetrabutylammonium perchlorate was used as an electrolyte when measuring. ITO was used as a working electrode and saturated Ag/AgNO$_3$ as a reference electrode. Ferrocene was a reference compound for potential calibration.

EL devices were fabricated as the following structure: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials (30 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (200 nm), where 2-TNATA was used as hole injection layer, NPB as hole transporting layer, Alq$_3$ as electron transporting layer, the synthesized materials as emitting layer, LiF as electron injection layer, ITO as anode and Al as cathode. The organic layer was vacuum-deposited using thermal evaporation at a vacuum base pressure of 10^{-6} torr and the rate of deposition being 1 Å/s to give an emitting area of 4 mm^2, and the aluminum layer was continuously deposited under the same vacuum condition. The current-voltage (I-V) characteristics of the fabricated EL devices were obtained by Keithley 2400 electrometer. Light intensity was obtained by Minolta CS-100A.

Synthesis

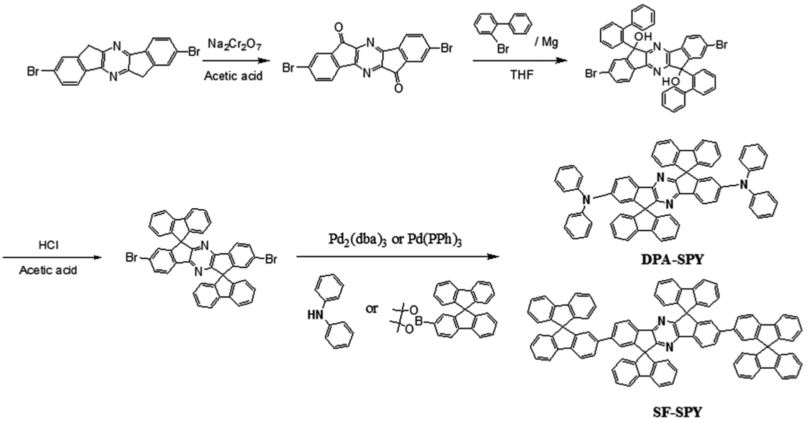
2,8-Bis(diphenylamine)-6,12-dihydrodiindeno[1,2-b:1,2-e]-6,12-bifluorenepyrazine (DPA-SPY). 2,8-Dibromo-6,12-dihydrodiindeno[1,2-b:1,2-e]-6,12-bifluorenepyrazine 0.50 g (0.70 mmol) and then diphenyl amine 0.26 g (1.53 mmol) were mixed in a round flask of 500 mL $Pd_2(dba)_3$ 0.02 g (0.021 mmol) was added, which was stirred by using anhydrous toluene of 300 mL as solvent. And $(t\text{-}Bu)_3P$ 0.047 g (0.21 mmol) added which heated to 50°C. And t-BuONa 0.20 g (2.1 mmol) added and refluxed. The reaction was checked with TLC, and when the reaction was completed, extraction was performed by using water and toluene, and moisture was removed by using anhydrous $MgSO_4$. After removing solvent, the reaction mixture was finally purified with silica-gel column chromatography method and recrystallization was performed with ethyl acetate; and as a result, pure yellow final compounds were obtained. The final yield was 36%. ^1H NMR (500 MHz, $CDCl_3$) δ(ppm) 7.82(d, 4H), 7.66(d, 2H), 7.38(t, 4H), 7.19(d, 4H), 7.07(t, 8H), 6.89(m, 18H), 6.48(s, 2H), FT-IR (KBr cm^{-1}): 3061, 1613, 1594, 1490, 1445, 1369, 1329, 1284, 1244, 1182, 1120, 1067, 827, 738, 696. Fab^+-Mass m/e: 891

2,8-Bis(9′,9″-spirobifluorene-2-yl)-6,12-dihydro-indeno[1,2-b:1,2-e]-6,12-bifluorene pyrazine(SF-SPY). 2,8-Dibromo-6,12-dihydrodiindeno[1,2-b:1,2-e]-6,12-bifluorene pyrazine 0.5 g (0.70 mmol) and 4,4,5,5-tetra-methyl-2-9H-spirobifluoren-2-yl-1,3,2-dioxaborolane 0.87 g (1.96 mmol) were mixed in a round flask of 500 mL and then tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$) 0.62 g (0.5 mmol) was added, which was stirred by using anhydrous THF of 300 mL as solvent. Afterwards, 2 M K_2CO_3 (100 mL) was added and refluxed. The reaction was checked with TLC, and when the reaction was completed, extraction was performed by using water and toluene, and moisture was removed by using anhydrous $MgSO_4$. After removing solvent, the reaction mixture was finally purified with silica-gel column chromatographic method and recrystallization was performed with THF and ethanol; and as a result, pure yellow final compounds were obtained. The final yield was 61%. ^1H NMR (500 MHz, THF-d_8): δ(ppm) 6.52(d, 2H), 6.59(d, 4H), 6.74(d, 4H), 6.87(d, 4H), 6.99(t, 6H), 7.08(t, 4H), 7.32(m, 6H), 7.37(m, 8H), 7.71(d, 2H), 7.83 ~ 7.78(m, 8H), 7.92(d, 4H), FT-IR (KBr cm^{-1}): 3020, 2920, 2860, 1710, 1610, 1510, 1440, 1360, 1220, 1170, 1120, 1070, 1020, 887, 827, 752, 729. Fab^+-Mass m/e: 1185.

Results and Discussion

In the locations 2 and 8 of indenopyrazine, which is the core group of blue emission, diphenylamine groups were introduced as the side groups as shown in Scheme 1 and it was compared with SF-SPY substituted with spirobifluorenyl groups on the locations 2 and 8.

Table 1 shows the optical properties of the synthesized DPA-SPY and SF-SPY: the UV-visible maximum absorptions of DPA-SPY and SF-SPY were 459 and 467 nm in solution and 422 and 423 nm in film respectively. There was a red shift by ca. 37 and 44 nm each in film. While SP-SPY has no discrepancy in the UV-visible maximum values between in solution and film, DPA-SPY was red-shifted by 8 nm in the film status. It is explained that since the dipole of DPA-SPY between molecules is bigger than that of SF-SPY, the interactions between molecules increase in film. In the PL spectra, DPA-SPY showed the maximum emissions of 492 and 507 nm both in solution and in film, and it was highly red-shifted by ca. 41 and 28 nm each, compared to 451 and 479 nm of SF-SPY. These results indicate that the introduction of diphenylamine groups on indenopyrazine core molecule as side groups reduced the band gap than that of spirobifluorene groups, because of the bipolar effect generated



Scheme 1. Chemical structures of the synthesized materials.

by donating of electrons of the diphenylamine group. SF-SPY, in which side group is spirobifluorenyl, has a longer conjugation length, so it is thought to induce molecular packing. Also, in the case of DPA-SPY, the small substituents as well as the electron donating effect of side group efficiently generate intermolecular packing which caused the red shift.

The electron distributions of HOMOs and LUMOs of the two molecules were explored by the AM-1 method of Spartan′04 program (Fig. 1) [7]. DPA-SPY had evenly distributed π-electrons in the phenyl group and N atom of diphenylamine under HOMO, compared to HOMO of SF-SPY. The high electron density in molecules means an easy oxidization of molecules, thereby leading to probable increase in HOMO levels.

Table 2 exhibits the HOMO and LUMO levels calculated from the edge results of CV and UV-visible experiments. The HOMO levels of DPA-SPY and SF-SPY were 5.44 eV and 6.00 eV, respectively and their band-gaps were 2.51 eV and 2.76 eV. In case of DPA-SPY, HOMO level was raised by 0.54 eV and band-gap was also narrowed by 0.25 eV than that of SF-SPY. It is because of that the side group of DPA-SPY, diphenylamine, has features of electron donating induced by non-pair electron. And DPA-SPY was expected to allow a relatively easy hole injection when devices are operated and to increase the mobility of holes because of the bipolar property of the electron donor-acceptor.

It has been reported that thermal properties of synthesized materials are in close relation with the lifetime of OLEDs [8]. The thermal properties of the synthesized ones were measured by TGA/DSC: as a result, T_m of the synthesized materials

Table 1. Optical properties of synthesized materials

	Solution (THF)		Film on glass	
	UV$_{max}$ (nm)	PL$_{max}$ (nm)	UV$_{max}$ (nm)	PL$_{max}$ (nm)
DPA-SPY	459	492	467	507
SF-SPY	422	451	423	464, 479

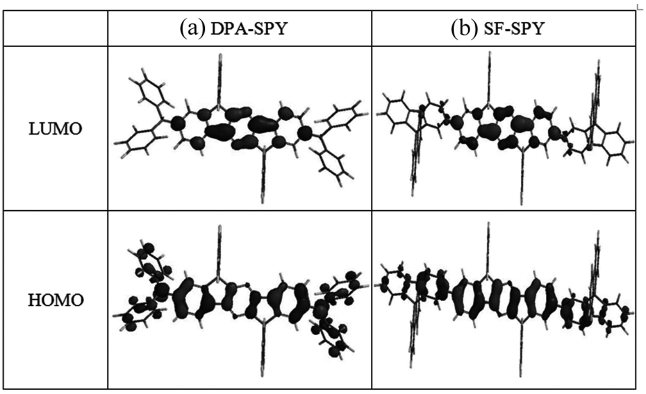


Figure 1. HOMOs and LUMOs of a) DPA-SPY and b) SF-SPY calculated at Semi-Empirical with a AM-1 basis set using Spartan′04.

was not all checked up to over 300°C and T_g could not be determined owing to its vague movement. It was also difficult to clearly find T_m even when thermal hysteresis was applied by multi-scan and the crystalline area was developed. It was thus thought that the materials are under amorphous state, as having least crystalline features and the materials of amorphous state would be fit for OLED as a constituent.

The synthesized DPA-SPY and SF-SPY were applied to non-doped OLED devices as emitting layers under the device configuration of ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials (30 or 40 nm)/Alq_3 (30 or 20 nm)/LiF (1 nm)/Al (200 nm). Figure 2 and Table 3 show the measured features of the devices.

As shown in Figure 2, DPA-SPY had an EL maximum value of 500 nm and FWHM of 49 nm, and SF-SPY had an EL maximum value of 480 nm and FWHM of 80 nm. Also in this figure, DPA-SPY exhibits a narrower spectrum than SF-SPY, which is caused by the relatively simple exciton transition, compared to SF-SPY. That is because SF-SPY additionally includes the chromophore of spirobifluorene in molecules while DPA-SPY has no additional effect of chromophore in the diphenylamine group. As the EL performance shown in Table 3, when DPA-SPY was used as an emitting material layer (EML) with the thickness of 30 nm and an electron transporting layer (ETL) was 30 nm in thickness, the EL spectrum included Alq_3 emission, limiting the recombination zone of the materials own. As mentioned above, that was resulted from the electron donation effect of DPA-SPY which increases HOMO levels and allows smooth injection and faster mobility of holes, thereby slightly moving the recombination center from EML to ETL. When the thickness of EML and ETL was changed to 40 and 20 nm to make up for the phenomenon above, the Alq_3 emission from ETL disappeared on the spectrum and a single EL spectrum of 500 nm was achieved. As for operating voltage, the

Table 2. Electrical and thermal properties of synthesized materials

Compounds	HOMO (eV)	LUMO (eV)	Band gap (eV)
DPA-SPY	5.44	2.93	2.51
SF-SPY	6.00	3.24	2.76

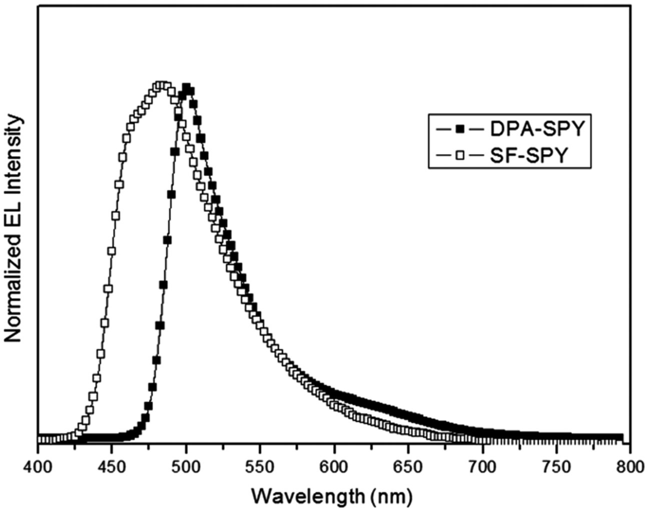


Figure 2. EL spectra of OLED device.

Table 3. EL performance of synthesized materials: ITO/2-TNATA (60 nm)/NPB (15 nm)/Synthesized materials (30 or 40 nm)/Alq_3 (30 or 20 nm)/LiF (1 nm)/Al (200 nm) at 10 mA/cm^2

Emitters	EL_{max} (nm)	Voltage (V)	Luminance Efficiency (cd/A)	Power Efficiency (lm/W)	CIE (x,y)
DPA-SPY (30/30)	499, 527	6.5	0.95	0.46	(0.314, 0.530)
DPA-SPY (40/20)	500	6.6	0.99	0.47	(0.288, 0.538)
SF-SPY	485	9.4	1.56	0.52	(0.218, 0.336)

voltage was decreased to 6.6 V in the DPA-SPY device because of the lower barrier of the electronic level of DPA-SPY than that of SF-SPY. Thus, an electron donor, the diphenylamine group was introduced to blue core materials, for the purpose of realizing green emission. In that case, the efficiency was somewhat low (ca. 1 cd/A). This is attributed to the imbalance between holes and electrons by more enhanced mobility and large injection of holes. It is therefore expected that green emitting materials for better performance of efficiency and color purity could be synthesized if a stronger electron donating group is applied in the side group and an electron accepting group is added to the core area.

Conclusion

A new core material of organic green emitters, indenopyrazine was applied with diphenylamine groups as an electron donor on both side groups, and bipolarity in the molecules was induced. The bipolar feature increased evenly the π-electron density in molecules, thus raising the HOMO level. Consequently, it lowered the operating voltage and enhanced green emission, so did not need an additional chromophore, thereby showing the EL spectrum with a narrow FWHM.

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