New Deep Blue Emitting Materials Based on Indenopyrazine Core with High Thermal Stability

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Abstract

We report the synthesis and electroluminescent properties of new aromatic compounds as emitting materials based on indenopyrazine, such 2,8-bis(3,5-diphenylphenyl)-6,6,12,12-tetraethyl-6,12-dihydrodiindeno[1,2-b:1',2'-e]pyrazine (DPP-EPY) and 2,8-bis(3',5'-diphenylbiphenyl-4-yl)-6,6,12,12-tetraethyl-6,12-dihydrodiindeno[1,2-b:1',2'-e]pyrazine (DPBP-EPY). DPP-EPY showed high thermal stability, narrow FWHM of 46 nm, luminous efficiency of 1.04 cd/A at current density of 10 mA/cm^2 and CIE coordinate of (0.161, 0.104).

1. Introduction

To realize full color OLEDs still requires high efficiency, thermal stability, long lifetime and pure color coordinates of organic materials emitting red, green and blue colors [1]. However, blue emitting materials have low efficiency and stability due to incorrect carrier balance between electrons and holes resulting from large different electronic levels between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [1]. Also, those materials require higher operating voltage compared to red or green emitting materials because of difficulty in injection of holes and electrons. Heat resulting from high voltage can damage the device and thereby greatly shorten the lifetime. So the thermal stability of materials is very important. Generally, it is difficult to get a pure deep blue color because full-width at half-maximum (FWHM) of emission spectra become broader by intermolecular interaction as the material moves from solution state to film state. This is a general behavior of the blue emitting materials and there are only a few materials with narrow FWHM. Therefore, a study on materials with high thermal stability and pure color coordinates is necessary [2, 3]. In this study, new heteroaromatic molecule, indenopyrazine as a core was used to increase thermal stability of materials and enhance color purity f or blue OLEDs. Two indenopyrazine derivatives 2,8-bis(3,5-diphenylphenyl)-6,6,12,12-tetraethyl-6,12-dihydrodiindeno [1,2 -b:1',2'-e]pyrazine (DPP-EPY) and 2,8-bis(3',5'-diphenylbiphenyl-4-yl)-6,6,12,12-tetraethyl-6,12-dihydrodiinde no[1,2-b:1',2'-e]pyrazine (DPBP-EPY) were synthesized as new deep blue emitting materials by breaking the planar structure of indenopyrazine core with introduction of bulky side group *m*-terphenyl and triphenylbenzene connected in *meta* position. Thermal stability, optical and electrical properties of the two materials were measured and compared, and the synthesized materials were used as emitting layer to develop non-doped OLED devices.

2. Experimental

2.1. General method

^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker, 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 HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo- and electro-luminescence spectroscopy. The melting temperatures (T_m), glass-transition temperatures (T_g), crystallization temperatures (T_c), and degradation temperatures (T_d) of the compounds

were measured by carrying out differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC2910 (TA Instruments) and thermogravimetric analysis (TGA) using a SDP-TGA2960 (TA Instruments). OELD devices were fabricated as the following structure: ITO / NPB (30nm) / TCTA (20nm) / synthesized materials (30nm) / Alq_3 (30nm) / LiF (1nm) / Al (200nm), where *N,N'*-bis(naphthalen-1-yl)-*N,N'*-bis(phenyl)benzidine (NPB), 4,4',4"-tri(*N*-carbazolyl)triphenylamine (TCTA) as hole transporting layer, 8-hydroxyquinoline aluminum (Alq_3) as electron transporting layer, the synthesized materials as emitting layers, lithium fluoride (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 1Å/s to give an emitting area of 4 mm^2, and the Al 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-1000.

2.2. General synthesis of new emitters.

These emitters were synthesized by Suzuki aryl-aryl coupling reaction using Pd catalyst. A typical synthetic procedure was as follows : To 2,8-dibromo-6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (1g, 1.9 mmol) and 4,4,5,5-Tetramethyl-2-[1,1';3',1"]terphenyl-5'-yl-[1,3,2]dioxaborolane (1.49g, 4.19 mmol) in a 500mL round-bottomed flask under a nitrogen atmosphere were added $Pd(OAC)_2$ (0.042g, 0.19 mmol), tri-cyclohexyl-phosphine (0.053g, 0.19 mmol) and toluene. The temperature was increased to 50 ℃, and tetraethylammonium hydroxide (13.5mL, 19.0 mmol, 20 wt % in water) was added. Stirring was continued at this temperature and the reaction was monitored by TLC. When the reaction was complete, extraction of the product was performed with water and toluene. The organic extract was dried with $MgSO_4$ added, and then filtered the solvent removed in vacuum. The resulting crude mixture was passed through a short-column of silica with THF as the eluent and then recrystallized from THF to obtain DPP-EPY as a white solid.

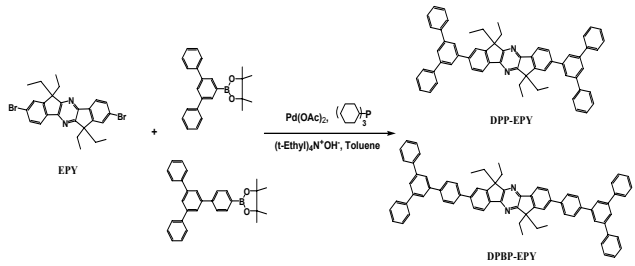
2.3. Synthesis of 2,8-bis(3,5-diphenylphenyl)-6,6,12,12-tetraethyl-6,12-dihydrodiindeno[1,2-b:1',2'-e]pyrazine (DPP-EPY)

The final yield was 90 %. ^1H NMR (500 MHz, $CDCl_3$) : δ (ppm) : 8.21 (d, 2H). 7.88 (s, 4H), 7.81 (m, 4H), 7.75 (m, 10H), 7.42 (t, 4H), 2.41 (m, 4H), 2.17 (m, 4H), 0.43 (t, 12H), ^{13}C NMR (300 MHz, $CDCl_3$) : 163.2, 152.2, 150.5, 142.8, 142.6, 142.3, 141.4, 138.9, 129.1, 127.8, 127.6, 127.0, 125.5, 122.0, 121.7, 54.3, 31.5, 9.0, FT-IR (KBr cm^{-1}) : 3056, 2960, 2929, 2875, 1594, 1496, 1455, 1371, 1288, 1221, 1178, 1124, 1029, 873, 840, 700, Fab^+-MS m/e : 825.

2.4 Synthesis of 2,8-bis(3',5'-diphenylbiphenyl-4-yl)-6,6,12,12-tetraethyl-6,12-dihydrodiindeno[1,2-b:1',2'-e]pyrazine (DPBP-EPY)

The final yield was 42%. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm) : 8.20 (d, 1H), 7.86 (t, 7H), 7.78 (d, 1H), 7.74 (d, 5H), 7.51 (t, 4H), 7.41 (t, 2H), 2.42 (m, 2H), 2.17 (m, 2H), 0.46 (t, 6H), ^{13}C NMR (300 MHz, $CDCl_3$) : 163.2, 150.5, 142.7, 142.0, 141.8, 141.3, 140.7, 140.5, 138.8, 129.1, 128.0, 127.9, 127.8, 127.6, 126.7, 125.2, 121.8, 121.7, 54.3, 31.5, 8.9, FT-IR (KBr cm^{-1}) : 3062, 2960, 2921, 2875, 1594, 1517, 1498, 1455, 1413, 1367, 1309, 1261, 1226, 1176, 1122, 1078, 1027, 919, 881, 831, 705, Fab^+-MS m/e : 976.

3. Results and discussion



Scheme 1. Synthetic routes of new chemical structures.

Two indenopyrazine derivatives DPP-EPY and DPBP-EPY were synthesized as new deep blue emitting materials by breaking the planar structure of indenopyrazine core with introduction of bulky side group *m*-terphenyl and triphenylbenzene connected in *meta* position. As shown in Figure1and Table 1, synthesized materials in solution state showed UV maximum value of 403nm and 409nm, respectively for DPP-EPY and DPBP-EPY. DPP-EPY was blue shifted further because conjugation length was shortened by one less phenyl in the side group. In addition, PL maximum in solution state was 428nm and 438nm in deep blue region. Full-width at half-maximum (FWHM) of these two materials was narrow at 45nm and 46nm. This suggests an

advantage of showing pure color coordinates in OLED devices. PL maximum value in film state was respectively 456nm and 460nm also in deep blue region, and FWHM represented sharp spectra with 46 and 52. Looking at the broadening of FWHM of EPY PL spectrum from 46 nm to 75 nm with change in the state from solution to film, side groups m-terphenyl and triphenylbenzene can be interpreted as effective in prevention of packing of molecules [2].

In particular, FWHM of DPP-EPY and DPBP-EPY in film state is narrow at 46 nm and 52 nm. Narrow FWHM resulted from reduction in intermolecular interaction with change in the state of material to film state and can be interpreted as the effect of bulky side group [4]. Especially, DPP-EPY shows a spectrum blue shifted more than DPBP-EPY, allowing a purer deep blue emission.

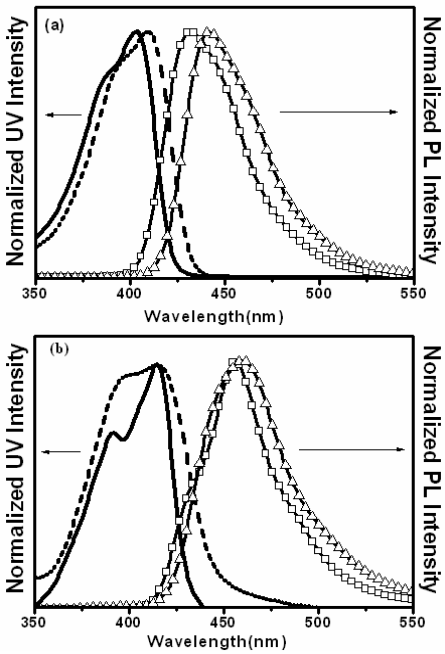


Figure 1. UV-Visible absorption and PL spectra (a) in THF solution (b) in film state : UV-Visible absorption spectra of DPP-EPY (line), DPBP-EPY (dash) and PL spectra of DPP-EPY (-□-), DPBP-EPY (-△-)

Table 1. Optical properties of synthesized materials.

Compounds	Solution[a]			Film on glass		
	UV_{max} (nm)	PL_{max} (nm)	FW HM (nm)	UV_{max} (nm)	PL_{max} (nm)	FW HM (nm)
DPP-EPY	404	428	45	415	456	46
DPBP-EPY	409	438	46	415	460	52

In order to verify thermal stability of synthesized materials, Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) were performed to measure Tg, Tc, Tm and Td summarized in Figure 2 and Table 2. Tg was not observed in DPP-EPY but was 154℃ in DPBP-EPY. Tm was 402℃ and 379℃ respectively and Tc of DPBP-EPY was found to be 277℃. Looking at the TGA/DSC result, high Tm suggested an excellent thermal stability [2]. Also, since Tg was only observed in DPBP-EPY, DPBP-EPY probably has a more amorphous property compared to DPP-EPY. Organic materials can be changed or damaged by heat during operation of devices, and thus thermal stability is important. This is closely related to the lifetime of OLED devices [5,6]. As a result, the synthesized materials are expected to show excellent lifetime of OLED devices due to excellent thermal stability.

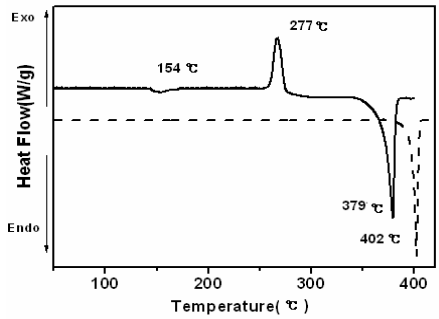


Figure 2. (a) Second DSC scan data after N_2 Treatment of DPP-EPY (dash) and DPBP-EPY (line), 10℃/min, N_2 condition.

Table 2. Thermal properties of synthesized materials.

Compounds	T_g/°C	T_c/°C	T_m/°C	T_d/°C
DPP-EPY	-	-	402	419
DPBP-EPY	154	277	379	449

T_g : glass transition temperature, T_c : crystallization temperature, T_m : melting-point temperature, T_d : decomposition temperature (5 % weight loss)

Non-doped OLED devices were developed using the synthesized materials as emitting layer. Luminance efficiency and power efficiency of DPP-EPY and DPBP-EPY were respectively 1.04, 0.61 cd/A and 0.27, 0.17 lm/W. DPP-EPY showed better

efficiency compared to DPBP-EPY. Both synthetic materials show deep blue spectrum with maximum emitting wavelength of about 450 ~ 460 nm. EL maximum value was blue shifted further in DPP-EPY at 452 nm than DPBP-EPY at 464 nm. This also results from the conjugation length of side group. Especially as also shown in film PL spectrum, EL spectrum was extremely narrow with FWHM of 46 nm. Accordingly, DPP-EPY showed CIE coordinate of (0.161, 0.104) in the deep blue region close to the National Television System Committee (NTSC), realizing excellent color coordinate and blue color as a new blue emitting material.

4. Summary

In this study, we successfully synthesized two new deep-blue emitters based on indenopyrazine derivatives by preventing intermolecular interaction from planar molecular structure with introduction of *m*-terphenyl and triphenylbenzene as bulky side groups in the new indenopyrazine core. As a result of measuring optical and thermal properties of two materials in solution and film states, both materials showed highly reduced intermolecular interaction and excellent thermal stability. Especially, very narrow FWHM was shown even in film state because intermolecular interaction was reduced by two bulky side groups. Synthesized materials were used as emitting layer to create non-doped OLED devices, realizing a deep blue OLED device with DPP-EPY close to NTSC blue standard with EL maximum of 452 nm and excellent CIE coordinates of (0.161, 0.104).

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5. References

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