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

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New deep blue emitting materials 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) were synthesized through introduction of *m*-terphenyl or triphenylbenzene bulky side groups in a new indenopyrazine core. These materials all showed high thermal stability and highly reduced intermolecular interaction. DPP-EPY and DPBP-EPY showed PL maxima of 456 nm and 460 nm in deep blue region and narrow PL spectra with full-width at half-maximum (FWHM) of 46 nm and 52 nm, respectively. As a result of making non-doped OLED devices using these synthesized materials as emitting layers, DPP-EPY showed EL spectrum of 452 nm, very narrow FWHM of 46 nm, luminance efficiency of 1.04 cd/A with current density of 10 mA/cm^2 and CIE coordinate of (0.161, 0.104), creating a deep blue OLED close to the National Television System Committee (NTSC) blue standard.

Keywords: Indenopyrazine, Blue Emitting Material, OLED, Fluorescence.

1. INTRODUCTION

After the report by Tang on green emitting organic light emitting device (OLED) with improved stability with formation of double-layer small molecule organic thin-films in 1987, efforts for development of OLED display using small molecule materials began in earnest.[1] Commercialization of full color display for such OLEDs requires high efficiency, thermal stability, long device lifetime and pure color coordinates of organic materials emitting red, green and blue colors.[2] According to reports by recent studies, blue emitting materials show low efficiency due to incorrect carrier balance between electrons and holes resulting from different electronic levels between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) because of large band gap.[2] Also, blue emitting materials require higher operating voltage compared to red or green emitting materials because of difficulty in injection of holes and electrons. On the other hand, heat resulting from high voltage can damage the device and shorten the lifetime. Therefore, thermal stability of material is important. It is also difficult to emit a pure deep blue color because full-width at half-maximum (FWHM) of photoluminescence (PL) and electroluminescence (EL) becomes broader with intermolecular interaction as the material moves from solution state to film state. This is a unique property of organic π-conjuated materials. Therefore, a study on materials with high thermal stability and pure blue color coordinates is necessary for full color OLEDs.[3,4]

In our previous study, indenopyrazine newly reported as a core material for blue OLED with excellent thermal property was used to increase thermal stability of materials.[3] In this study, 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-dihydrodiindeno[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 groups such as *m*-terphenyl or triphenylbenzene connected in 2,8 position. These materials include not only different new side groups of biphenyl benzene and triphenyl benzene, but also different link position compared to previous material, TP-EPY including meta-terphenyl side group.[3] In here, we compare the optical- and electrical property according to conjugation length of new side group. Thermal stability, optical and electrical properties of the two materials were measured

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and compared, and the synthesized materials were used as emitting layer in non-doped OLED devices.

2. EXPERIMENTAL DETAILS

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 (30 nm)/TCTA (20 nm)/synthesized materials (30 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (200 nm), 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 1 Å/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 (1 g, 1.9 mmol) and 4,4,5,5-Tetramethyl-2-[1,1′;3′,1″]terphenyl-5′-yl-[1,3,2]dioxaborolane (1.49 g, 4.19 mmol) in a 500 mL round-bottomed flask under a nitrogen atmosphere were added Pd(OAC)$_2$ (0.042 g, 0.19 mmol), tri-cyclohexyl-phosphine (0.053 g, 0.19 mmol) and toluene. The temperature was increased to 50 °C, and tetraethylammonium hydroxide (13.5 mL, 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 vacuo*. 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)

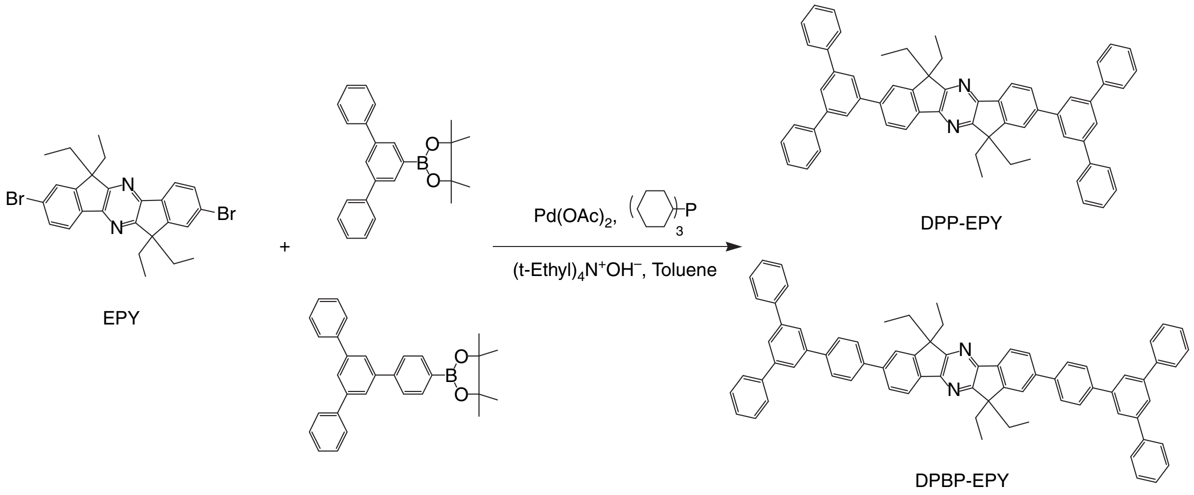
The final yield was 90%. ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm): 8.21 (d, 2H). 7.88 (s, 4H), 7.81 (m, 4H), 7.75 (m, 10H), 7.42 (t, 4H), 2.41 (m, 4H), 2.17 (m, 4H), 0.43 (t, 12H), ^{13}C NMR (300 MHz, CDCl$_3$): 163.2, 152.2, 150.5, 142.8, 142.6, 142.3, 141.4, 138.9, 129.1, 127.8, 127.6, 127.0, 125.5, 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%. ^{1}H 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

Synthetic processes of DPP-EPY and DPBP-EPY are summarized in Scheme 1. Four ethyl groups were introduced in positions 6 and 12 of indenopyrazine core through tetraalkylation of dibromoindenopyrazine to form dibromo-tetraethylindenopyazine (EPY). And then, DPP-EPY and DPBP-EPY were synthesized through Suzuki Ar–Ar coupling reaction of borated m-terphenyl or triphenylbenzene with EPY dibrominated at positions 2 and 8. Synthesized materials were refined with silica gel column chromatography and the structure was verified with ^{1}H-NMR, ^{13}C-NMR, FT-IR and Fab$^+$-mass. Optical properties of these two materials in the solution state and thin-film state were summarized in Figure 1 and Table I. As shown in Figure 1(a), synthesized materials in solution state showed UV maximum wavelengths of 404 nm and 409 nm, respectively for DPP-EPY and DPBP-EPY. DPP-EPY was blue-shifted slightly because conjugation length



Scheme 1. Synthetic routes of new chemical structures.

was shortened by one less phenyl unit in the side group. In addition, PL maxima of DPP-EPY and DPBP-EPY in solution state were 428 nm and 438 nm in deep blue region, respectively. Full-width at half-maximum (FWHM) of these two materials was narrow at 45 nm and 46 nm. This suggests an advantage of showing pure color coordinates in OLED devices. PL maximum value in film state was respectively 456 nm and 460 nm also in deep blue region, and FWHM represented sharp spectra with 46 and 52 nm. Looking at the broadening of FWHM of tetraethyl indenopyrazine 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.[3]

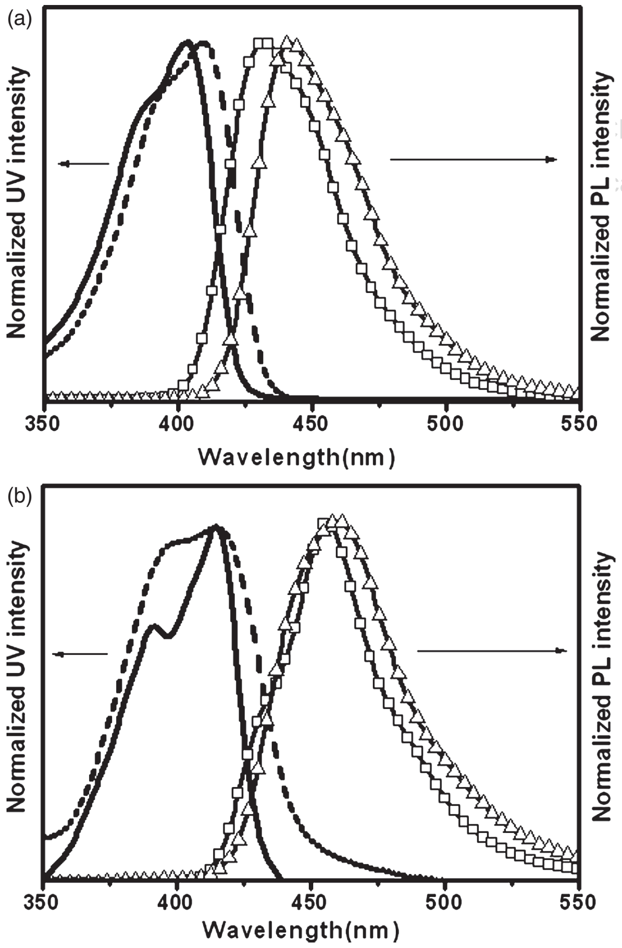


Fig. 1. UV-Visible absorption and PL spectra (a) in THF solution (b) in film state: UV-Visible absorption spectra of DPP-EPY (line), DPBP-EPY (dash) and PL spectra of DPP-EPY (-□-), DPBP-EPY (-Δ-).

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. Especially, DPP-EPY shows a spectrum blue shifted more than DPBP-EPY, allowing a purer deep blue emission.[6]

In order to verify thermal stability of synthesized materials, thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to measure T_g, T_c, T_m and T_d summarized in Figure 2 and Table II. T_g was not observed in DPP-EPY but was 154 °C in DPBP-EPY. T_m was 402 °C and 379 °C respectively and T_c of DPBP-EPY was found to be 277 °C.

Looking at the TGA/DSC result, high T_m suggested an excellent thermal stability.[2] Also, since T_g was only observed in DPBP-EPY, DPBP-EPY probably has a more amorphous property compared to DPP-EPY. Organic

Table I. Optical properties of synthesized materials.

	Solution[a]			Film on glass		
Compounds	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

[a] Solution in THF($1.0*10^{-6}$ M).

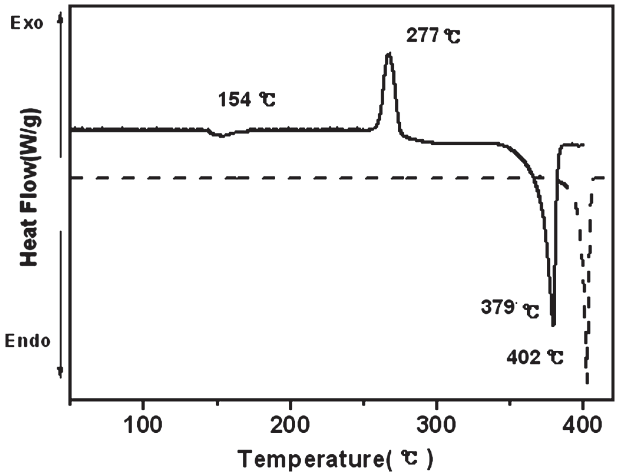


Fig. 2. Second DSC scan data after N_2 Treatment of DPP-EPY (dash) and DPBP-EPY (line), 10 °C/min, N_2 condition.

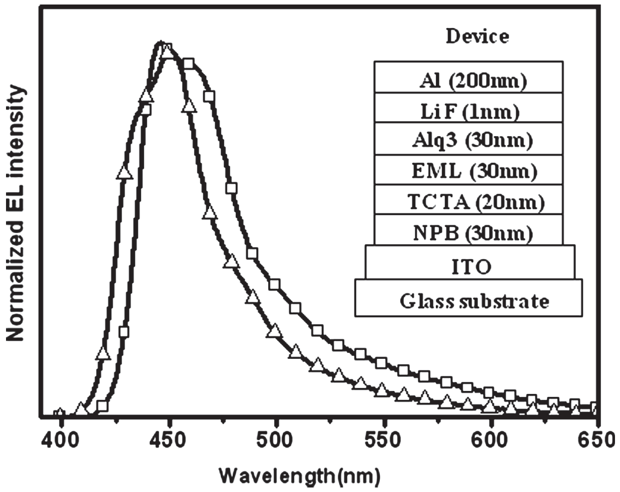


Fig. 3. EL spectra of OLED device using synthesized EML. The insert shows OLED device structure (DPP-EPY (-□-), DPBP-EPY (-Δ-)).

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(b), 7] As a result, the synthesized materials are expected to show more extended lifetime of OLED devices due to excellent thermal stability.

Non-doped OLED devices were developed using the synthesized materials as emitting layer. Structure of device is ITO/NPB (30 nm)/TCTA (20 nm)/synthesized materials (30 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (200 nm). As summarized in Table III, 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 efficiencies compared to DPBP-EPY. Figure 3 shows the EL spectra of the OLED devices. Both synthetic materials show deep blue spectra with maximum emitting wavelengths of about 450∼460 nm. EL maximum wavelength was blue shifted further in DPP-EPY at 452 nm than DPBP-EPY at 464 nm.

This also results from the shorten conjugation length of side group. Especially as shown in film PL spectrum of DPP-EPY, the EL spectrum was also extremely narrow with FWHM of 46 nm. Accordingly, DPP-EPY showed excellent CIE coordinate of (0.161, 0.104) in the deep blue region close to the National Television System Committee (NTSC) blue standard.

Table II. 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).

Table III. EL performance of synthesized materials: ITO/NPB (30 nm)/TCTA (20 nm)/Synthesized materials (30 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (200 nm) at 10 mA/cm^2.

Emitters	EL_{max} (nm)	FW HM (nm)	Luminance efficiency (cd/A)	Power efficiency (lm/W)	CIE (x, y)
DPP-EPY	452	46	1.04	0.27	(0.161, 0.104)
DPBP-EPY	464	50	0.61	0.17	(0.179, 0.159)

4. CONCLUSION

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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