

Synthesis and Electroluminescence Properties of Novel Deep Blue Emitting 6,12-Dihydro-diindeno[1,2-b;1',2'-e]pyrazine Derivatives

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Abstract

We report the synthesis of blue emitting materials with a new core structure containing indenopyrazine. Non-doped device using one of these materials as a blue emitter was found to exhibit high external quantum efficiency of 4.6% and excellent color purity of (0.154, 0.078) as well as narrow emission band of 47nm FWHM.

1. Introduction

In recent, the range of applications of functional organic materials has rapidly expanded, with especially innovative uses discovered in the field of optoelectronics.¹ Researchers have begun to report how the properties of functional organic materials can be modified by varying their core and side groups.² A key research area is thus the development of new core and side groups and the study of how they combine in functional organic materials. In this study, we designed and synthesized a new core system, which we tested in organic light-emitting diodes (OLEDs).³

In this study, We report the synthesis of new blue emitting materials, 6,6,12,12-tetraethyl-2,8-bis(9',9''-spirobifluorene-2-yl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (SF-EPY), 6,6,12,12-tetraethyl-2,8-bis-[1,1';3',1'']terphenyl-4'-yl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (TP-EPY), 6,6,12,12-tetraethyl-2,8-(10-phenyl-9-anthracyl)-6,12-dihydrodiindeno(1,2-b;1,2-e)pyrazine (PA-EPY), and 6,6,12,12-tetraethyl-2,8-bis-(10-naphthalen-2-yl-anthracen-9-yl)-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (NA-EPY). Synthesized materials show that good color purity and superior thermal properties was synthesized for the

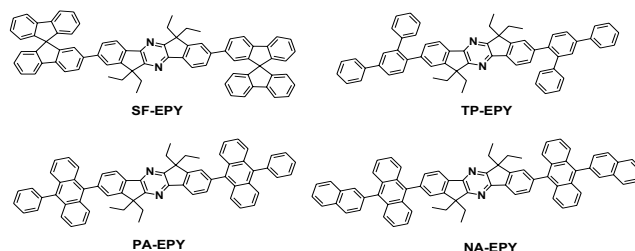
first time and used as the core component of new blue OLED materials, and their optical, thermal, and electroluminescence properties were examined.⁴

2. Experimental

2.1. Synthesis

2.1.1. General synthesis of SF-EPY, TP-EPY, PA-EPY, and NA-EPY

These compounds were synthesized by Suzuki aryl-aryl coupling reaction using Pd catalyst. A typical synthetic procedure was as follows : 2,8-dibromo-6,6,12,12-tetraethyl-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (6.7 g, 13 mmol) and 4,4,5,5-tetramethyl-2-9H-spirobifluorene-2-yl-1,3,2-dioxaborolane (13 g, 31 mmol) were mixed in a round flask of 500 mL and then tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄) (1.5g, 1.3 mmol) was added, which was stirred by using anhydrous THF of 350 mL as solvent. Afterwards, 2M K₂CO₃ (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 EA (ethyl acetate), and moisture was removed by using anhydrous MgSO₄. After removing solvent, recrystallization was performed with THF and ethanol



Scheme 1. Synthetic routes of synthesized materials.

2.1.2. 6,6,12,12-tetraethyl-2,8-bis(9',9''-spirobifluorene-2-yl)-6,12-dihydrodiindeno[1,2-b:1,2-e]pyrazine (SF-EPY)

The final yield was 35%. ¹H NMR (500 MHz, THF-d₈) : δ 0.29 (t, 12H), 2.07 (m, 4H), 2.30 (m, 4H), 6.62 (d, 2H), 6.74 (d, 4H), 7.11 (m, 8H), 7.37 (m, 6H), 7.50 (d, 2H), 7.64 (s, 2H), 7.80 (d, 2H), 7.94 (m, 8H), 8.03 (d, 2H). ¹³C NMR(500MHz, CDCl₃) : 163.0, 152.1, 150.3, 149.6, 148.9, 142.1, 142.0, 141.3, 138.5, 128.1, 127.9, 127.5, 126.7, 124.4, 124.1, 122.8, 121.6, 121.3, 120.5, 120.3, 54.2, 31.4, 29.9, 8.8. FT-IR (KBr cm⁻¹) : 3061, 2962, 2928, 2875, 1713, 1614, 1446, 1367, 776, 752, 730. FAB⁺-MS *m/e* : 997, High-resolution mass spectra (HRMS) Calcd. for C₇₆ H₅₇ N₂ (M⁺) 997.4522, found : 997.4512.

2.1.3. 6,6,12,12-Tetraethyl-2,8-bis-[1,1';3',1'']terphenyl-4'-yl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (TP-EPY)

The yield was 56%. ¹H NMR (500 MHz, THF-d₈) : δ (ppm) 0.20 (t, 12H), 1.83 (s, 4H), 2.17 (s, 4H), 7.1 (s, 2H), 7.27 (m, 10H), 7.35 (t, 2H), 7.48 (m, 6H), 7.63 (d, 2H), 7.74 (m, 8H), 7.95 (d, 2H), ¹³C NMR(500MHz, CDCl₃) : 162.9, 152.2, 149.1, 142.2, 141.8, 141.4, 140.8, 140.7, 139.9, 137.9, 131.2, 130.1, 129.7, 129.0, 128.3, 127.7, 127.4, 126.9, 126.4, 125.5, 121.0, 53.9, 31.3, 8.9. FT-IR(KBr cm⁻¹) : 3060, 2962, 2930, 2873, 1713, 1613, 1478, 1441, 1369, 830, 773, 749, 697. FAB⁺-MS *m/e* : 824, HRMS Calcd for C₆₂ H₅₂ N₂ (M⁺) 824.4130, found : 824.4124.

2.1.4. 6,6,12,12-tetraethyl-2,8-(10-Phenyl-9-anthracyl)-6,12-dihydrodiindeno(1,2-b;1,2-e)pyrazine(PA-EPY)

The yield was 24 %. ¹H-NMR (500 MHz, CDCl₃): δ (ppm) 0.63 (t, 12H), 2.25 (s, 4H), 2.50 (s, 4H), 7.39 (m, 8H), 7.64-7.61 (m, 10H), 7.77 (d, 4H), 7.83 (d, 4H), 7.95 (d, 2H), 8.01 (d, 2H), 8.05 (d, 2H), 8.11 (d, 2H), 8.41 (d, 2H). FT-IR(KBr cm⁻¹) : 3059, 2961, 2928, 2875, 1714, 1614, 1456, 1441, 1364, 821, 763, 747. FAB⁺-MS *m/e* : 973, HRMS Calcd for C₇₄ H₅₇ N₂ (M⁺) 973.4522, found : 973.4508.

2.1.5. 6,6,12,12-Tetraethyl-2,8-bis-(10-naphthalen-2-yl-anthracen-9-yl)-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine(NA-EPY)

The yield was 24 %. ¹H-NMR (500 MHz, CDCl₃): δ (ppm) 0.63 (t, 12H), 2.25 (s, 4H), 2.50 (s, 4H), 7.39 (m, 8H), 7.64-7.61 (m, 10H), 7.77 (d, 4H), 7.83 (d, 4H), 7.95 (d, 2H), 8.01 (d, 2H), 8.05 (d, 2H), 8.11 (d, 2H), 8.41 (d, 2H). FT-IR(KBr cm⁻¹) : 3059, 2961, 2928, 2875, 1714, 1614, 1456, 1441, 1364, 821, 763, 747. FAB⁺-MS *m/e* : 973, HRMS Calcd for C₇₄ H₅₇

N₂ (M⁺) 973.4522, found : 973.4508.

2.2. General methods

¹H and ¹³C NMR spectra were recorded on Bruker Avance 500 and Avance 600 spectrometers. Fast atom bombardment (FAB) Mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained with a HP 8453 UV-VIS-NIR spectrometer. A Perkin Elmer luminescence spectrometer LS50 (xenon flash tube) was used for photo- and electro-luminescence spectroscopy. For the EL devices, all organic layers were deposited under 10⁻⁶ Torr, with a rate of deposition of 1 Å/s to give an emitting area of 4 mm². The LiF and aluminium layers were continuously deposited under the same vacuum conditions. The current-voltage (I-V) characteristics of the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-100A and CS-1000A.

3. Results and discussion

The UV-Visible maximum absorption wavelengths of the four synthesized materials, SF-EPY, TP-EPY, PA-EPY, and NA-EPY in solution are in the range 400~420 nm and the maximum wavelengths of the PL spectra are in the blue region near 450 nm (see Table 1). In addition, the PL spectra of films of these materials were found to be around 10 nm red-shifted with respect to those of their solutions. 10 nm is a relatively small red shift, which could be due to the suppression of the intermolecular π-π* stacking of Indenopyrazine(IPY) by the introduction of bulky side groups. Further, in the case of TP-EPY, the PL maximum wavelength is 450 nm for both solution and film, as shown in Figure 1. The FWHM (full width at half maximum) values are 47 nm for the solution state and 54 nm for the solid state; these widths are narrower than those of other blue emitting materials.

Table 1. Optical and electrical properties of synthesized compounds.

Compounds	Solution (THF)		Film on Glass			HOMO (eV)	
	UV _{max} [nm]	PL _{max} [nm]	UV _{max} [nm]	PL _{max} [nm]	FWHM		
SF-EPY	416	447	468	401, 414	452, 473	52	5.90
TP-EPY	398	450	400	450	54	6.04	
PA-EPY	385, 400	450	385	400	458	56	5.69
NA-EPY	385, 401	455	385	405	468	87	5.60

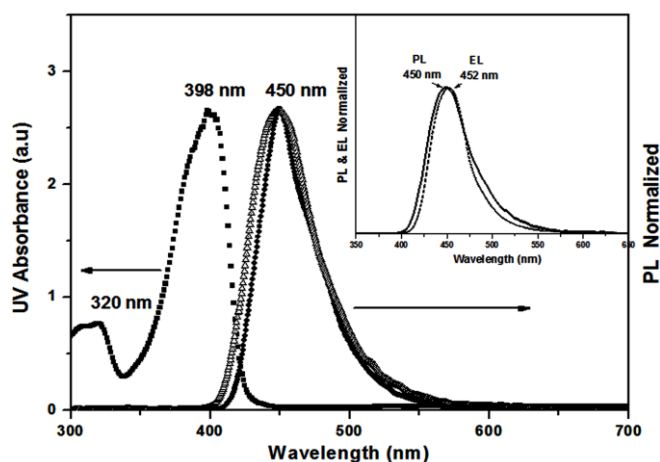


Figure 1. UV-Visible (■) and PL spectra (solution: ●, film: △) of TP-EPY (UV: 6.06×10^{-5} M, PL: 4.85×10^{-4} M in THF). The inset shows the EL (dash) and PL film (line) spectra.

The synthesized materials and DPVBi were used as the emitting layers (EMLs) in OLEDs with the following structure: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials or DPVBi (30 or 40 nm)/Alq₃ (30 or 20 nm)/LiF (1 nm)/Al (200 nm). The OLED properties were then measured and the results are summarized in Table 2.

Compounds	EL _{max} (nm)	Voltage (V)	Luminance Efficiency (cd/A)	Power Efficiency (lm/W)	C. I. E. (x,y)
SF-EPY ^a	458, 469	8.5	2.62	0.96	(0.152, 0.142)
TP-EPY ^a	452	7.5	2.01	0.92	(0.154, 0.078)
PA-EPY ^a	466	7.8	4.11	1.66	(0.194, 0.247)
NA-EPY ^a	474, 505	7.9	4.25	1.69	(0.273, 0.417)
NA-EPY ^b	469, 499	9.6	3.95	1.29	(0.229, 0.329)
DPVBi ^a	467	8.6	3.59	1.31	(0.153, 0.167)

a: Emitting Material (30 nm)/Alq₃ (30 nm)

b: Emitting Material (40 nm)/Alq₃ (20 nm)

Table 2. EL performance of the synthesized compounds: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials or DPVBi (30 or 40 nm)/Alq₃ (30 or 20 nm)/LiF (1 nm)/Al (200 nm) at 10 mA/cm².

The EL spectra of the devices with SF-EPY, TP-EPY, and PA-EPY as emitting layers were found to be almost identical to the PL spectra. In the case of the NA-EPY device, electroluminescence at both 505 nm and 474 nm was observed, and it was thought that this luminescence was due to the NA-EPY and Alq₃ interface. In order to confirm this, a new device was

fabricated with a NA-EPY (40 nm)/Alq₃ (20 nm) structure. In this device, electrons pass relatively quickly through the thin electron transporting layer (ETL), which generates additional recombination centers in the emitting layer. As a result, the EL intensity at 499 nm was found to be significantly weakened, and thus the emission at 505 nm in the original device is due to the Alq₃ interface, and arises because hole movement in NA-EPY is faster than in the other synthesized materials. Even though the PA-EPY and NA-EPY non-doped devices exhibit a high efficiency of about 4 cd/A, their CIE coordinates were found to be (0.194, 0.247) and (0.229, 0.329) respectively, i.e., in the sky-blue region, because the EL spectra of these two materials are broad. The SF-EPY and TP-EPY non-doped devices were found to exhibit luminescence efficiencies of 2.62 and 2.01 cd/A respectively. Interestingly, the absolute PL quantum efficiency of the film in TP-EPY is only 58.7% of that of DPVBi, but its EL external quantum efficiency (E.Q.E.) is 114% (at 10 mA/cm²) and 93% (at 100 mA/cm²) higher than that of the DPVBi device. Further, the EL maximum wavelengths of the SF-EPY and TP-EPY devices are 458 and 452 nm, respectively, i.e., in the deep blue region, with CIE coordinates (0.152, 0.142) and (0.150, 0.078) respectively, which is a purer blue than obtained with DPVBi (0.153, 0.167). Especially, non-doped device of TP-EPY showed 4.6% of E.Q.E and CIE(0.15, 0.078) with 47nm FWHM(see Figure 2). As shown in Figure 1, TP-EPY in particular has an EL maximum wavelength that is almost the same as its PL maximum wavelength at 452 nm in the deep blue region; thus this material produces a very pure deep blue.

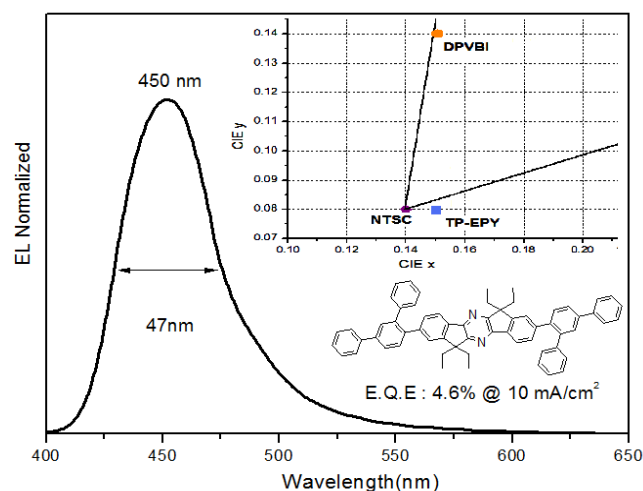


Figure 2. Normalized EL Spectrum of ITO/2-TNATA/NPB/TP-EPY/Alq₃ /LiF/Al devices at 10 mA/cm².

4. Summary

In summary, we have for the first time synthesized and utilized an indenopyrazine derivative as a core moiety in different functional organic materials. Non-doped devices using these materials as blue emitters were found to exhibit high luminance efficiencies of up to 2.01~4.3 cd/A at a current density of 10 mA/cm². The CIE coordinates of TP-EPY were found to be excellent with a Y-axis value less than 0.08, (0.150, 0.078), which are almost the same as the standard blue CIE coordinates of the National Television Standards Committee (NTSC). Furthermore, these synthesized materials exhibit excellent thermal properties that should improve the lifetimes of OLED devices. In particular, TP-EPY exhibits properties that are superior to those of the commercialized emitting material DPVBi, particularly with regards to its morphological stability and CIE coordinates.

5. References

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