

New Blue Emitting Indenopyrazine Derivatives for OLEDs : Improving the EL Properties Through Substitution Effects by Using Terphenyl Side Group

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Abstract

New blue emitting materials of *o,p*-TP-EPY and *m,m*-TP-EPY were synthesized using two terphenyl units with different structures in the new core of indenopyrazine. EL spectrum of *o,p*-TP-EPY was more blue shifted than *m,m*-TP-EPY, and external quantum efficiency of *o,p*-TP-EPY was showed improvement of about 60% compared to efficiency of *m,m*-TP-EPY.

1. Introduction

Organic light-emitting diodes (OLED) are receiving the spotlight as next generation flat screen display among optoelectronic fields based on π -conjugated organic molecule, and many studies are recently being conducted on them.¹ For realization of full color in such OLEDs, red, green and blue-emitting materials with excellent performance are necessary. However, blue emitting material accompanies serious problems of low efficiency and shorter lifetime compared to red or green emitting material due to difficulty in hole and electron injection with larger band gap.²

Most of π -conjugated materials used as blue emitting materials until now make use of fluorene, bifluorene and anthracene as core.³ Also in order to create a highly efficient and pure blue emitting material for OLED using these molecules as core, our research team minimized intermolecular interactions through introduction of a bulky side group to prevent unwanted bathochromic effect on wavelength and reduction of luminescence efficiency.²

Accordingly, a systematic study on molecular structure that can effectively prevent intermolecular interactions is needed for the material to be used as a

highly efficient and pure blue emitting material.

Therefore, the purpose of this study was to introduce two terphenyl groups as bulky aromatic side groups to indenopyrazine for reduction of intermolecular interaction to the maximum possible extent and to report the results of a systematic research on the influence of minute changes in molecular structure according to the type of terphenyl group on intermolecular interactions and OLED characteristics.⁴

2. Experimental

2.1. General method

¹H-NMR spectra were recorded on Bruker, Advance 300 and 500, 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 (EL) 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). OLED devices were fabricated as the following structure: ITO/NPB (30nm)/TCTA (20nm)/synthesized materials (30nm)/Alq₃ (30nm)/LiF (1nm)/Al (200nm), where, *N,N'*-bis(naphthalen-1-yl)-

N,N'-bis(phenyl)benzidine [NPB] as hole injection layer, 4,4',4''-tri(*N*-carbazolyl)triphenylamine [TCTA] was hole transporting and exciton blocking layer, 8-hydroxyquinoline aluminum [Alq₃] 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 mm², and the Al layer was continuously deposited under the same vacuum condition. The current-voltage (I-V) characteristics of the fabricated OLED devices were obtained by Keithley 2400 electrometer. Light intensity was obtained by Minolta CS-1000A.

2.2. General syntheses 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-4'-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°C, 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 MgSO₄ 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 *o,p*-TP-EPY as a white solid.

2.3. Synthesis of 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 (*o,p*-TP-EPY)

The yield was 56 %. ¹H-NMR (500 MHz, THF-d₈) : δ (ppm) 0.20 (t, 12H), 1.70 (m, 4H), 2.17 (m, 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 (500 MHz, 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

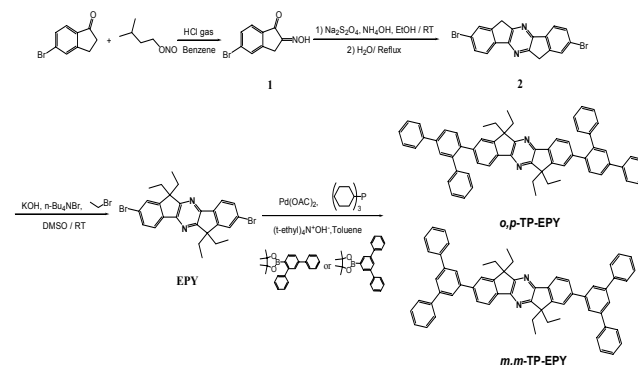
2.4 Synthesis of 6,6,12,12-tetraethyl-2,8-bis-

[1,1';3',1'']terphenyl-5'-yl-6,12-dihydro-diindeno[1,2-*b*;1',2'-*e*]pyrazine (*m,m*-TP-EPY)

The yield was 90%. ¹H-NMR (500 MHz, CDCl₃) : δ (ppm) 0.43(t, 12H), 2.17(m, 4H), 2.41(m, 4H), 7.42(t, 4H), 7.52(t, 8H), 7.75(m, 10H), 7.81(m, 4H), 7.88(s, 4H), 8.21(d, 2H). ¹³C- NMR (300 MHz, CDCl₃) : 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, 1288, 1221, 1178, 1124, 1029, 873, 840, 700, Fab⁺-MS *m/e* : 825.

3. Results and discussion

As shown by Scheme 1, in case of indenopyrazine core, bromo-indenopyrazine can be synthesized by using 5-bromo-indanone as starting material, dropping isoamylnitrite in acid conditions, synthesizing with oxime and then performing cyclization. Since positions 6 and 12 of the synthesized bromo-indenopyrazine are acidic, diethyl-indenopyrazine (EPY) can be synthesized through dialkylation. Then *o,p*-TP-EPY and *m,m*-TP-EPY can be synthesized through Suzuki Ar-Ar coupling with the two borated *m*-terphenyl groups as side groups.⁴ Synthesized materials were refined using silica-gel column chromatography and the structure was verified using NMR, FT-IR and Fab⁺-mass analyses.



Scheme 1. Synthetic routes of new blue emitting materials (*o,p*- : two phenyls at terphenyl side group of indenopyrazine core system were substituted in *ortho* and *para* positions; *m,m*- : both phenyls were substituted in *meta* position)

UV-visible absorption and photoluminescence (PL) spectra of the synthesized materials in solution and thin film states are summarized in Figure 1 and Table 1. As shown in Figure 1 (a), UV-visible spectra of both synthesized materials in solution state showed maximum absorption wavelengths of about 400 nm and similar absorption edges. This can be interpreted as two materials having similar effective π -conjugation lengths regardless of substituting position

of two *m*-terphenyl substituted to indenopyrazine core as side groups. PL spectra also show maximum emission wavelengths of about 430 nm in the deep blue region. However, as shown in Table 1 and Figure 1 (b), while UV-visible absorption spectra in film state only show a slight difference ($\Delta = 7$ nm) between *o,p*-TP-EPY and *m,m*-TP-EPY respectively with 408 nm and 415 nm, PL spectra show larger difference ($\Delta = 13$ nm) with 443 nm and 456 nm. On one hand, as a result of comparing PL spectrum in solution state and film state, *o,p*-TP-EPY showed a red shift of 9 nm and *m,m*-TP-EPY was further red shifted by 28 nm (See Table 1). This seems to have resulted from easier intermolecular interaction in *m,m*-TP-EPY compared to *o,p*-TP-EPY when the state changes from solution to film.

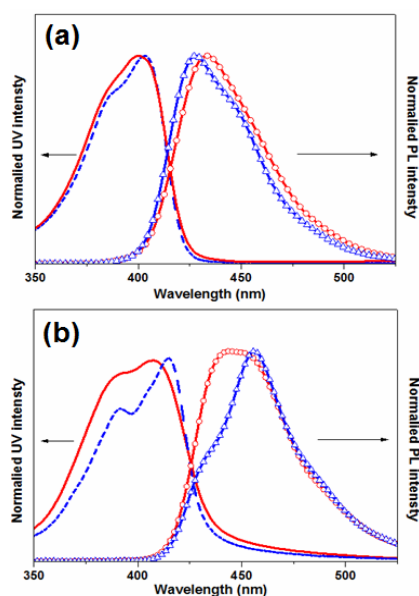


Figure 1. (a) UV-Visible absorption and PL spectra in THF solution (b) in film state : UV-Visible absorption of *o,p*-TP-EPY (red line), *m,m*-TP-EPY (blue dash) and PL of *o,p*-TP-EPY (\circ), *m,m*-TP-EPY (\triangle)

Table 1. Optical properties of synthesized materials.

Compounds	Solution ^a		Film on glass	
	UV _{max} (nm)	PL _{max} (nm)	UV _{max} (nm)	PL _{max} (nm)
<i>o,p</i> -TP-EPY	403	434	408	443
<i>m,m</i> -TP-EPY	404	428	415	456

a. solution in THF (1.0×10^{-6} M)

In order to explain this, changes of PL spectra according to concentration in THF solution, in which both synthesized materials well dissolve, were measured (see Figure 2). As a result, fluorescence increases in *o,p*-TP-EPY until the concentration reached from 10^{-6} to 10^{-4} M and rapidly reduces at 10^{-3} M due to intermolecular interaction. Maximum

wavelength was also about 10 nm red shifted from 434 nm to 444 nm. However in case of *m,m*-TP-EPY, reduction in fluorescence due to intermolecular interaction occurs as a lower concentration than *o,p*-TP-EPY at 10^{-4} M with a 10 nm red shift. Thus, such result suggests that *o,p*-TP-EPY more effectively prevents intermolecular interaction compared to *m,m*-TP-EPY.

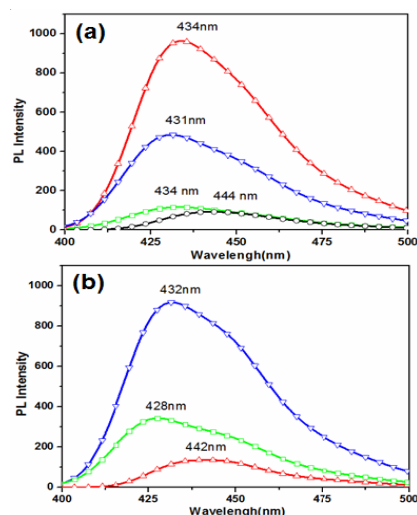


Figure 2. PL spectrum at different frequencies (a) *o,p*-TP-EPY, (b) *m,m*-TP-EPY : 1.0×10^{-6} M (\square), 10^{-5} M (∇), 10^{-4} M (\triangle), 10^{-3} M (\circ) in THF solution.

Thermal properties of synthesized materials were measured using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and the measurement results are summarized in Table 2. As a result, *o,p*-TP-EPY and *m,m*-TP-EPY respectively showed T_m of 337 and 402 °C. In case of T_g , while *o,p*-TP-EPY showed 129 °C, several thermal scans were unable to find T_g value of *m,m*-TP-EPY. Such value is a profound increase of over two times the value of T_g for the commercial blue emitting material 4,4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl (DPVBi) at 64 °C ($T_m = 204$ °C).⁴ Since such thermal stability can be interpreted as smaller morphological changes in materials due to heat during operation of OLED device, large improvement in OLED device lifetime is anticipated. Also, looking at the fact that T_g value is shown by *o,p*-TP-EPY and not observed in *m,m*-TP-EPY with higher T_m for *m,m*-TP-EPY, *o,p*-TP-EPY is expected to have a relatively more amorphous solid state.

Table 2. Thermal properties of synthesized materials.

Compounds	T_g /°C	T_c /°C	T_m /°C	T_d /°C
<i>o,p</i> -TP-EPY	129	167	337	441

m,m-TP-EPY - - 402 419

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

Lastly, synthesized materials were used as emitting material layer to manufacture a non-doped OLED device with the following structure: ITO/ NPB(30nm)/ TCTA(20nm)/ synthesized emitters (30nm)/ Alq₃(30nm)/ LiF(1nm)/ Al(200nm). EL properties are summarized in Table 3. EL spectrum corresponds well to PL spectrum in film state and larger blue shift was shown by *o,p*-TP-EPY ($\lambda_{\max, EL} = 440$ nm) than *m,m*-TP-EPY ($\lambda_{\max, EL} = 452$ nm) as expected (see Figure 3). In addition, CIE coordinates respectively were (0.156, 0.078) and (0.161, 0.104) with *o,p*-TP-EPY showing a color coordinate of deeper blue region compared to *m,m*-TP-EPY. External quantum efficiency (E.Q.E) of devices was 2.68 and 1.61 % for *o,p*-TP-EPY and *m,m*-TP-EPY, respectively. Efficiency of *o,p*-TP-EPY was improved more by over 60 % compared to *m,m*-TP-EPY. As shown in the optical property experiment earlier, such results can be explained as a larger improvement in EL performance by more efficient prevention of intermolecular interaction when two phenyls at terphenyl side group of indenopyrazine core system were substituted in *ortho* and *para* positions in comparison to when both phenyls were substituted in *meta* position.

Table 3. EL performances of synthesized emitters : ITO/NPB (30nm)/TCTA (20nm)/Emitters (30nm)/Alq₃ (30nm)/ LiF (1nm)/ Al (200nm) at 10 mA/cm².

Emitters	EL _{max} (nm)	Luminance Efficiency (cd/A)	Power Efficiency (lm/W)	E.Q.E ^a (%)	CIE ^b (x,y)
<i>o,p</i> -TP-EPY	440	1.17	0.30	2.68	(0.156, 0.078)
<i>m,m</i> -TP-EPY	452	1.04	0.27	1.61	(0.161, 0.104)

a : External Quantum Efficiency, b : 1931 Commission International de l'Eclairage

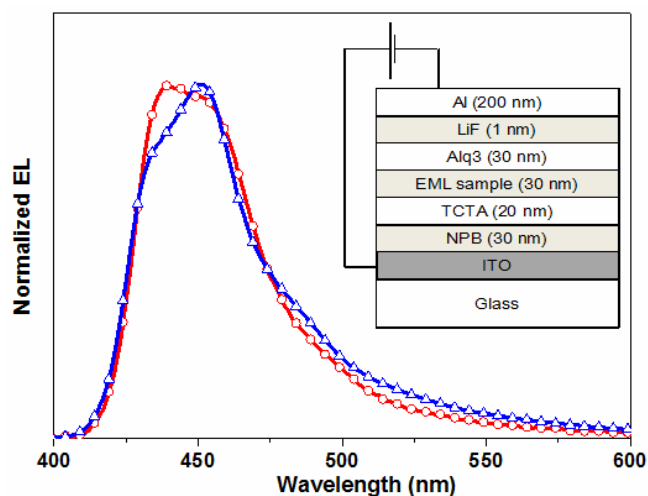


Figure 3. EL spectra of OLED devices using synthesized emitters : *o,p*-TP-EPY (○) and *m,m*-TP-EPY (△). The insert shows OLED device structure.

4. Summary

Two blue emitting materials were synthesized using *o,p*-TP-EPY and *m,m*-TP-EPY where two bulky *m*-terphenyl aromatic side groups were introduced at different substitution position in the new core system of indenopyrazine (IPY). When comparing optical properties of the synthesized materials in the solution state or thin film state and at various concentrations *o,p*-TP-EPY with two phenyls of terphenyl substituted in *ortho* and *para* positions more effectively prevented intermolecular interaction than *m,m*-TP-EPY with two phenyls substituted in *meta* position. Such phenomenon was also reflected well in the OLED device experiment. With application of synthesized materials as emitter in non-doped OLED device, EL maximum wavelength was more blue shifted in *o,p*-TP-EPY (440 nm) compared to *m,m*-TP-EPY (452 nm) and efficiency was increased over 60% more in *o,p*-TP-EPY than *m,m*-TP-EPY with E.Q.E of 2.68 and 1.61%, respectively.

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5. References

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