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# New blue-violet emitters based on an indenopyrazine core for OLEDs: Effects of the position of *m*-terphenyl side group substitution on optical and electroluminescence properties

Youngil Park<sup>a</sup>, Sookang Kim<sup>a</sup>, Ji-Hoon Lee<sup>b</sup>, Dong Hyun Jung<sup>c</sup>, Chung-Chih Wu<sup>d</sup>, Jongwook Park<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry/Display Research Center, The Catholic University of Korea, Bucheon 420-743, Republic of Korea

<sup>b</sup> Department of Polymer Science and Engineering and Photovoltaic Technology Institute Chungju National University, Chungju-si, Chungbuk 380-702. Republic of Korea

<sup>c</sup> Insilicotech Co. Ltd., Kolontripolis, 210, Geumgok-Dong, Seongnam, Gyeonggi-Do, Republic of Korea

<sup>d</sup> Department of Electrical Engineering, Graduate Institute of Electro-Optical Engineering and Graduate Institute of Electronics Engineering, National Taiwan University, Taipei, Taiwan 10617, PR China

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# ABSTRACT

A promising class of blue-violet emitters based on a new functional core, the indenopyrazine group, has successfully been synthesized for the first time by substitution with bulky *m*-terphenyl side groups in the *ortho*, *meta*, or *para* positions. There are larger blue shifts in the *UV-visible* absorption and PL spectra of the synthesized *ortho*- and *para*-substituted derivatives than in those of the *meta*-substituted derivative. Molecular calculations verified that these differences are due to the variation in the  $\pi$ -conjugation length of the derivatives with the position at which the side group is attached to the indenopyrazine core. When the synthesized compounds were used as emitting layers in non-doped OLED devices, a related trend was observed in their optical properties. In particular, the OLED containing the *para*substituted derivative was found to exhibit excellent characteristics, with maximum EL emission at 423 nm, a full width at half maximum of 42 nm, pure violet emission with CIE coordinates (0.173, 0.063), and an external quantum efficiency of 1.88%.

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#### 1. Introduction

The interest in organic functional materials based on  $\pi$ conjugated molecules has been rapidly growing in diverse fields. Many remarkable results have been reported, especially in the field of optoelectronics (organic light-emitting diodes [OLEDs], solar cells, and organic thin-film transistors [OTFTs]) [1–7]. Many researchers are engaged in ongoing efforts to systematically elucidate the correlation between their molecular structures and properties, with the aim of developing materials with good performance and stability for particular optoelectronic applications.

The synthesis of 6,12-dihydro-diindeno[1,2-b;1',2'e]pyrazine (indenopyrazine) was first reported by Ebel and Deuschel in 1956, but no follow-up studies examined the derivatives and potential applications of this molecule [8]. Given the intense current interest in organic functional materials based on aromatic compounds such as fluorene, bifluorene, and anthracene for use in OLEDs in next-generation flat panel displays, new core structures could potentially yield materials with improved physical properties for diverse applications [9–28]. We recently reported new derivatives based on an indenopyrazine core structure that could be used as blue emitters in OLEDs.



<sup>\*</sup> Corresponding author. Tel.: +82 2164 4821; fax: +82 2 2164 4764. *E-mail address:* hahapark@catholic.ac.kr (J. Park).

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These compounds were found to exhibit a high external quantum efficiency of 4.6% and a pure deep blue emission with CIE coordinates (0.154, 0.078) [29]. In other research in this area, Yamashita's group used an indenopyrazine derivative, difluoro-diindeno[1,2-b;1',2'-e]pyrazine-6,12-dione, as the channel material in an n-type OTFT, with excellent results (mobility, 0.17 cm<sup>2</sup>/Vs; on/off ratio, 10<sup>7</sup>) [30]. Indenopyrazine is therefore gaining recognition in optoelectronics as a potentially useful core structure for a new family of organic functional materials. However, if indenopyrazine derivatives with enhanced performance suitable for diverse optoelectronics applications are to be developed, more systematic studies of their structures and properties must be conducted.

In a previous study, we hypothesized that the  $\pi - \pi$ stacking of molecules in the thin-film state due to the plate-like molecular structure of indenopyrazine would give rise to a reduction in its fluorescence yield and a bathochromic effect on its emission wavelength. To remove this effect, we introduced short alkyl groups at the 6- and 12positions of indenopyrazine and a bulky *m*-terphenyl side group at positions 2 and 8. An OLED device based on the resulting molecule was found to exhibit excellent characteristics, with high efficiency and a pure deep blue color [29]. In this study, we investigated the effects on the optical and electroluminescence properties of varying the substitution position of the side groups (Scheme 1). In particular, we examined the bulky *m*-terphenyl substitution positions 2 and 8 (meta positions), 1 and 7 (ortho positions), and 3 and 9 (para positions).

Although varying the substitution positions of side groups on emitting cores offers important information about the intrinsic properties of the molecules, it is difficult to change the side group substitution positions for most emitting cores (*e.g.* fluorene, bifluorene and anthracene) [9–28]. In this study, however, varying the substitution pattern was facilitated by the use of bromo-indanones with Br substituted at positions 4, 5, and 6 as the starting compounds. This procedure enabled the facile synthesis of three compounds in which *m*-terphenyl is substituted at the *ortho, meta*, and *para* positions: 6,6,12,12-tetraethyl-1,7-bis-[1,1';3',1"]terphenyl-4'-yl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (*o*-TP-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 (*m*-TP-EPY), and 6,6,12,12-tetra

raethyl-3,9-bis-[1,1';3',1"]terphenyl-4'-yl-6,12-dihydrodiindeno[1,2-b;1',2'-e]pyrazine (*p*-TP-EPY).

#### 2. Experimental

#### 2.1. Synthesis of o-, m-, and p-TP-EPY

The compounds o-, m-, and p-TP-EPY were synthesized following literature procedures [29]: 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-4'-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), tricyclohexylphosphine (0.053 g, 0.19 mmol) and toluene. The temperature was then 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, the product was extracted with water and toluene. The organic extract was dried over anhydrous MgSO<sub>4</sub> and filtered, after which 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 m-TP-EPY as a white solid. The purification method of oand *p*-TP-EPY was same as *m*-TP-EPY.

# 2.1.1. Synthesis of 6,6,12,12-tetraethyl-1,7-bis-[1,1';3',1"] terphenyl-4'-yl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (o-TP-EPY)

The final yield was 1.06 g, 68%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.00–7.99 (d, 2H), 7.74–7.72 (m, 6H), 7.59 (d, 2H), 7.48–7.45 (t, 4H), 7.41–7.36 (m, 12H), 7.16–7.14 (m, 4H), 7.08 (s, 2H), 2.10 (m, 2H), 1.85 (m, 2H), 1.74 (m, 2H), 1.62 (m, 2H), 0.27–0.20 (m, 6H), –0.51 to –0.60 (m, 6H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): 162.7, 152.5, 145.4, 141.5, 141.1, 140.9, 139.0, 138.4, 134.1, 131.7, 130.7, 129.6, 129.1, 128.2, 127.8, 127.4, 126.9, 126.5, 125.0, 120.4, 56.2, 30.6, 30.1, 8.9, 8.8, 7.8. FT-IR (KBr cm<sup>-1</sup>): 3056, 2961, 2928, 2873, 1599, 1486, 1469, 1456, 1400, 1367, 1291, 1244, 1204, 1182, 1103, 1076, 1030, 776, 755, 742, 698. HRMS Calcd for C<sub>62</sub>H<sub>53</sub>N<sub>2</sub> (M+H)<sup>+</sup>, 825.4209, found: 825.4229.



Scheme 1. Chemical structures of o-, m-, and p-TP-EPY.

2.1.2. Synthesis of 6,6,12,12-tetraethyl-3,9-bis-[1,1';3',1"] terphenyl-4'-yl-6,12-dihydro-diindeno[1,2-b;1',2'-e]pyrazine (p-TP-EPY)

The final yield was 0.89 g, 57%. <sup>1</sup>H NMR (500 MHz, THFd<sub>8</sub>):  $\delta$  (ppm) 8.09–7.76 (s, 2H), 7.76–7.75 (m, 8H), 7.71– 7.69 (d, 2H), 7.46–7.43 (t, 4H), 7.35–7.34 (t, 2H), 7.27– 7.22 (m, 6H), 7.19–7.15 (m, 6H), 7.04–7.03(d, 4H), 2.47– 2.28 (m, 4H), 2.06–1.99 (m, 4H), 0.38–0.36 (t, 12H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): 162.9, 152.4, 148.0, 141.7, 141.3, 140.9, 140.7, 140.6, 139.8, 139.5, 131.7, 131.3, 130.2, 129.4, 129.0, 128.0, 127.6, 127.3, 126.8, 126.3, 122.4, 122.2, 53.8, 31.3, 8.8. FT-IR (KBr cm<sup>-1</sup>): 3055, 3025, 2962, 2919, 2874, 2853, 1599, 1486, 1462, 1442, 1317, 1288, 1233, 1178, 1124, 895, 826, 763, 748, 697, 486, HRMS Calcd for C<sub>62</sub>H<sub>53</sub>N<sub>2</sub> (M+H)<sup>+</sup>, 825.4209, found: 825.4214.

# 2.1.3. Synthesis of 1,7-dibromo-6,6,12,12-tetraethyl-6,12dihydro-diindeno[1,2-b;1',2'-e]-pyrazine (1c)

2.1.3.1. 4-Bromo-2,3-dihydro-2-(hydroxyimino)indene-1-one (1a). The yield was 79%. <sup>1</sup>H NMR (300 MHz, acetone-d<sub>6</sub>):  $\delta$  (ppm) 11.90 (s, 1H), 7.95–7.92 (d, 1H), 7.79–7.76 (d, 1H), 7.50–7.45 (t, 1H), 3.76 (s, 2H).

2.1.3.2. 1,7-Dibromo-6,12-dihydro-diindeno[1,2-b;1',2'e]pyrazine (1b). The yield was 56%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.17–8.15 (d, 2H), 7.65–7.63 (d, 2H), 7.45–7.42 (d, 2H), 4.02 (s, 4H).

2.1.3.3. 1,7-Dibromo-6,6,12,12-tetraethyl-6,12-dihydrodiindeno[1,2-b;1',2'-e]pyrazine (1c). The yield was 38%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.08–8.05 (d, 2H), 7.58– 7.56 (d, 2H), 7.32–7.29 (t, 2H), 2.72–2.55 (m, 4H), 2.37– 2.29 (m, 4H), 0.27–0.24 (t, 12H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): 163.0, 152.2, 145.9, 142.5, 142.3, 134.1, 133.9, 129.4, 129.3, 128.5, 120.4, 120.2, 119.8, 57.5, 57.4, 28.3, 8.8. Fab<sup>+</sup>-MS *m*/*e*: 526.

# 2.1.4. Synthesis of 3,9-dibromo-6,6,12,12-tetraethyl-6,12dihydro-diindeno[1,2-b;1',2'-e]pyrazine (3c)

2.1.4.1. 6-Bromo-2,3-dihydro-2-(hydroxyimino)indene-1-one (3a). The yield was 77%. <sup>1</sup>H NMR (300 MHz, acetone-d6):  $\delta$  (ppm) 11.83 (s, 1H), 7.89–7.85 (m, 2H), 7.64–7.61 (d, 1H), 3.82 (s, 2H).

2.1.4.2. 3,9-Dibromo-6,12-dihydrodiindeno[1,2-b:1,2e]pyrazine (3b). The yield was 53%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.37–8.36 (s, 2H), 7.64–7.60 (d, 2H), 7.54–7.38 (d, 2H), 4.04 (s, 4H).

2.1.4.3. 3,9-Dibromo-6,6,12,12-tetraethyl-6,12-dihydrodiindeno[1,2-b;1',2'-e]-pyrazine (3c). The yield was 63%. <sup>1</sup>H NMR (500 MHz, CDCl3):  $\delta$  (ppm) 8.23–8.21 (s, 2H), 7.58– 7.56 (d, 2H), 7.33–7.26 (d, 2H), 2.33–2.28 (m, 4H), 2.06– 2.02 (m, 4H), 0.38–0.33 (t, 12H), <sup>13</sup>C NMR(300 MHz, CDCl3): 163.1, 151.8, 148.5, 141.1, 132.3, 124.9, 124.6, 121.7, 54.1, 31.2, 8.7. Fab<sup>+</sup>-MS *m*/e: 526.

# 2.2. Measurements

The structures of the synthesized compounds were characterized by using NMR, FT-IR, and fast-atomic bom-

bardment (FAB) mass spectrometry. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 300 and Avance 500 spectrometers. The FT-IR spectra were recorded on a Thermo Electron Nicolet IR-200 spectrometer, FAB-mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The melting temperatures  $(T_m)$ , glasstransition temperatures  $(T_{\sigma})$ , 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 with a DSC2910 (TA Instruments) and thermogravimetric analysis (TGA) with a SDP-TGA2960 (TA Instruments). 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 electroluminescence spectroscopy. The redox potentials of the compounds were determined with cyclic voltammetry (CV) by using a WBCS 3000 system with a scanning rate of 100 mV/s. We used a synthetic material coated ITO as the working electrode, a saturated Ag/ AgNO<sub>3</sub> reference electrode, and acetonitrile (AN) with 0.1 M tetrabutylammonium perchlorate (TBAP) as the electrolyte. Ferrocene was used for potential calibration and for reversibility criteria.

#### 2.3. Fabrication of the OLEDs

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 mm<sup>2</sup>. In these devices, 4,4',4"-tris(N-(2-naphthyl)-Nphenyl-amino)-triphenylamine [2-TNATA] was used as the hole injection layer, N,N'-bis(naphthalen-1-yl)-N,N'bis(phenyl)benzidine [NPB] and 4,4',4"-tri(N-carbazolyl)triphenylamine [TCTA] were used as the hole transporting and exciton blocking layers, respectively, and 8hydroxyquinoline aluminum [Alq<sub>3</sub>] was used as the electron transporting layer [31]. The LiF and aluminum layers were continuously deposited under the same vacuum conditions. The device structures were ITO/2-TNATA (30 nm)/NPB (10 nm)/TCTA (10 nm)/o- or m- or p-TP-EPY (30 nm)/Alq<sub>3</sub> (30 nm)/LiF (1 nm)/Al (200 nm). 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-1000A.

#### 2.4. Computational details

The HOMO and LUMO energy levels of the indenopyrazine derivatives were optimized by using the DMol<sup>3</sup> program of Materials Studio 4.3<sup>®</sup>, which carries out quantum mechanical calculations with density functional theory (DFT). The Perdew, Burke and Ernzerhof (PBE) functional and double numeric polarization basis set was used in the calculations. The structures were optimized by using delocalized internal coordinates; to confirm that each optimized conformation was the minimum structure we performed numerical frequency analysis.

### 3. Result and discussion

#### 3.1. Synthesis and characterization

The indenopyrazine derivatives were synthesized according to literature procedures [29]. As shown in Scheme 2, we used bromo-indanones with Br substituted at positions 4, 5, and 6 as the starting compounds. In the first step, the oximes (1a, 2a, 3a) were synthesized via the reaction with isoamylnitrile dropped in under acid conditions. The oximes were then cyclized to synthesize the key intermediate dibromo-indenopyrazines (1b, 2b, 3b) with bromine present at the ortho, meta, and para positions in high yield (overall yield approximately 40%). Since the 6- and 12-position carbons of the synthesized dibromo-indenopyrazines are acidic, these carbons were capped with four ethyl groups (1c, 2c, 3c), and then the tetraethylated dibromo-indenopyrazines were coupled with a borated *m*-terphenyl group by carrying out Suzuki Ar-Ar coupling reactions. This procedure enabled the facile synthesis of o-, m-, and p-TP-EPY, in which m-terphenyl is substituted at the ortho, meta, and para positions respectively. The structures of the synthesized compounds were characterized by using NMR, FT-IR, and FAB-mass analysis.

## 3.2. Optical and electrochemical properties

The UV-visible absorption (Abs) spectra and photoluminescence (PL) spectra for the solution states of o-, m-, and p-TP-EPY are shown in Fig. 1, and the spectral features are summarized in Table 1. The PL quantum yields of the solution states of m-TP-EPY, p-TP-EPY, and o-TP-EPY were determined to be 73%, 61%, and 42%, respectively. As shown in Fig. 1, the Abs peaks of o-TP-EPY and p-TP-EPY were found to be blue-shifted 17 and 15 nm with respect to that of *m*-TP-EPY. In the PL spectra, the maxima for *o*-TP-EPY (411 nm) and *p*-TP-EPY (415 nm) were blue-shifted 26 and 22 nm, respectively with respect to that of *m*-TP-EPY at 437 nm, thereby moving these spectra from the blue region to the violet region. These findings suggest that changing the substitution position alters the intrinsic optical properties of the molecule.

These phenomena were also observed for the thin-film states, as shown in Fig. 2: the Abs peaks of o-TP-EPY (389 nm) and p-TP-EPY (390 nm) are blue-shifted 19 and 18 nm with respect to that of *m*-TP-EPY (408 nm), and the PL spectra maxima of o-TP-EPY (418 nm) and p-TP-EPY (426 nm) are blue-shifted 25 and 17 nm, respectively with respect to that of *m*-TP-EPY at 443 nm. Moreover, the minute differences of 6-11 nm between the PL spectral values of the solution and thin-film states for each derivative indicate that the short alkyl chains (ethyl) at carbon positions 6 and 12 of indenopyrazine and the *m*-terphenyl side groups on the aromatic rings effectively suppress the  $\pi$ - $\pi$ \* stacking of the molecules regardless of whether the substitution pattern is ortho, meta, or para. In addition, the full widths at half maximum (FWHMs) of the PL spectra for the thin-film state are 43 nm for o-TP-EPY and p-TP-EPY, but 54 nm for *m*-TP-EPY. The sharper spectra of *o*-TP-EPY and *p*-TP-EPY probably arise because these molecules have fewer electron transition states than *m*-TP-EPY.

The energy bands, and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of *o*-, *m*-, and *p*-TP-EPY were estimated with cyclic voltammetry (CV) and through absorption edge analysis by using a plot of (hv) vs.  $(\alpha hv)^2$ , where  $\alpha$ , *h*, and *v* are the absorbance, Planck's constant, and the frequency of light; the results are summarized in Table 1 [23]. The HOMO levels of *o*-TP-EPY and *p*-TP-EPY are 6.13 and 6.07 eV, respectively, which are slightly lower by 0.10



Scheme 2. Synthetic routes for o-, m-, and p-TP-EPY.



**Fig. 1.** Normalized UV and PL spectra of *o*-TP-EPY ( $\blacksquare$ ), *m*-TP-EPY ( $\bigcirc$ ), and *p*-TP-EPY (▲) in CHCl<sub>3</sub> (1.00 × 10<sup>-5</sup> M) solution.

and 0.04 eV, respectively than the HOMO level of *m*-TP-EPY at 6.03 eV. The band gaps of *o*-TP-EPY and *p*-TP-EPY were found to be 0.21 and 0.24 eV wider, respectively than that of *m*-TP-EPY.

#### 3.3. Theoretical calculations

In an attempt to theoretically explain the observed variations in the optical and electronic properties of the indenopyrazine core system with the substitution position

Table 1		
Optical and electrica	l properties of the synthesized	compounds

of the *m*-terphenyl side group, we performed frontier molecular orbital calculations to determine the electron density distributions of ethyl indenopyrazine (EIP-core), and o-, m-, and p-TP-EPY (Fig. 3). The structures of the indenopyrazine derivatives were optimized by using the DMol<sup>3</sup> program of Materials Studio 4.3<sup>®</sup>, which carries out quantum mechanical calculations with density functional theory (DFT). The Perdew, Burke and Ernzerhof (PBE) functional and double numeric polarization basis set was used in the calculations [32-34]. The most remarkable result obtained from the molecular orbital analysis is that the lobe of the orbital at the junction points of the ortho and para positions of the EIP-core and side groups is smaller than the lobe of the orbital at the junction point of the meta position, in both the HOMO and LUMO as shown in Fig. 3. In particular, a node was found at the junction points of the ortho and para positions for the HOMO and the LUMO. Therefore, whereas there is an extension of the conjugation in *m*-TP-EPY from the EIP-core to the *m*-terphenyl group, the nodes observed for *o*-TP-EPY and p-TP-EPY indicate that these molecules are less conjugated than *m*-TP-EPY. This difference in conjugation means that the energy gaps decrease in the order o-TP-EPY > p-TP-EPY > m-TP-EPY, as shown in Table 1. In addition, this trend explains the spectral phenomena shown in Fig. 1, such as the larger blue shift in the Abs and PL spectra induced by substitution of the *m*-terphenyl group at the ortho and para positions, and the wider band gaps. These findings establish that the  $\pi$ -conjugation of the indenopyrazine derivatives can be adjusted by placing side groups at the node or lobe of the electron distribution of the indenopyrazine core system (Fig. 3(a)). Thus, in efforts to develop optoelectronics devices based on  $\pi$ -conjugated molecules, physical characteristics such as their optical and electronic properties can be systematically controlled according to the electron density distribution of the orbital at the position where the side group attaches to the molecular core.

#### 3.4. Thermal properties

The thermal properties of the synthesized substances were determined by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results are summarized in Table 2. The  $T_m$  values of the synthesized *o*-, *m*-, and *p*-TP-EPY derivatives were found to be 365, 338, and 317 °C, respectively, which are more than 110 °C higher than the  $T_m$  of the commercial blue luminous material 4.4'-bis(2.2-diphenylvinyl)-1.1'-biphenyl (DPVBi),

	$UV_{max}^{a}(nm)$	$PL_{max}^{a}(nm)$	Q.Y <sup>b</sup> (%)	$UV_{max}^{c}(nm)$	$PL_{max}^{c}(nm)$	FWHM <sup>c</sup>	HOMO (eV)	LUMO (eV)	$\Delta E_{\exp}^{d}$ (eV)	$\Delta E_{cal} = (eV)$
o-TP-EPY	386	411	42	389	418	43	6.13	3.02	3.11	2.56
p-TP-EPY	388	415	73 61	390	443 426	54 43	6.07	2.99	3.08	2.53

 $^a\,$  Solution in CHCl\_3 (1.00  $\times$  10^–5 M).

<sup>b</sup> Q.Y. (quantum yield) was measured by using a calibrated integrating sphere system [38,39].

<sup>c</sup> Film on glass.

<sup>d</sup> Experimental band gaps.

<sup>e</sup> Band gaps obtained with frontier molecular orbital calculations.



**Fig. 2.** Normalized UV–Vis and PL spectra of thin-films of *o*-TP-EPY ( $\blacksquare$ ), *m*-TP-EPY ( $\bigcirc$ ), and *p*-TP-EPY ( $\land$ ).

which is 204 °C. The  $T_g$  values of *m*-TP-EPY and *p*-TP-EPY are 129 and 127 °C, respectively, which are approximately twice as high as that of DPVBi, 64 °C [29]. In the case of a thin-film of *m*-TP-EPY, the average surface roughness ( $R_a$ ) measured with atomic force microscopy (AFM) was found to undergo almost no change in comparison to that of a DPVBi film after storage at 65 °C for 24 h [29]. Improved lifetimes of the synthesized substances in OLED devices are anticipated [35].

#### 3.5. Electroluminescence properties

To determine whether the changes with substitution position in the intrinsic molecular properties are reflected in OLED (a representative optoelectronics device) performance, non-doped OLED devices were fabricated with the synthesized compounds as the emitting material layer (EML). The results are summarized in Table 3 and Fig. 4. The most important observation is that the electroluminescence (EL) spectra of *o*-TP-EPY and *p*-TP-EPY have maxima at 419 and 423 nm, respectively, which are blueshifted 21 and 17 nm with respect to the peak for *m*-TP-EPY at 440 nm (see Fig. 4). This trend in the EL spectra is



**Fig. 3.** Electronic density distributions of the frontier molecular orbitals (HOMO and LUMO) of the EIP-core (a), and of o-, *m*-, and *p*-TP-EPY (b).

**Table 2**Thermal properties of o-, m-, and p-TP-EPY.

	$T_{g}$ (°C)	$T_{\rm c}$ (°C)	$T_{\rm m}~(^{\circ}{\rm C})$	$T_{\rm d}$ (°C)
o-TP-EPY	-	-	365	403
m-TP-EPY	129	167	338	441
p-TP-EPY	127	165	317	442

in good agreement with the shifts from the blue region to the violet region observed in the PL spectra of the thin-films. In addition, the EL spectra of o-TP-EPY and p-TP-EPY are sharper than the *m*-TP-EPY EL spectrum, as reflected in the FWHMs (43 and 42 nm for o-TP-EPY and p-TP-EPY, respectively, compared to 47 nm for *m*-TP-EPY). Such narrow emission spectra can result in pure colors, which is advantageous for emitting materials. In terms of the Commission Internationale de l'Eclairage (CIE) coordinates, the y-axis values of o-TP-EPY and p-TP-EPY are 0.068 and 0.063 that is, closer to the violet region than the value of 0.078 for *m*-TP-EPY. These CIE coordinates show that adjusting the  $\pi$ -conjugation by varying the junction position of the side group attached to the indenopyrazine core system changes the optical and electronic properties, and that such changes can be exploited in OLEDs. The EL devices were found to exhibit power efficiencies and external quantum efficiencies (EQE). in the ranges 0.16-0.9 lm/W and 1.2-4.6%, respectively, at  $10 \text{ mA/cm}^2$  (see Table 3). The EQE of the *m*-TP-EPY device

#### Table 3

EL performances of multi-layered devices with the synthesized emitters. Device: ITO/2-TNATA (30 nm)/NPB (10 nm)/TCTA (10 nm)/o- or *m*- or *p*-TP-EPY (30 nm)/Alq<sub>3</sub> (30 nm)/LiF (1 nm)/Al (200 nm) at 10 mA/cm<sup>2</sup>.

Compounds	Volt (V)	L.E. <sup>a</sup> (cd/A)	P.E. <sup>b</sup> (1m/W)	E.Q.E. <sup>c</sup> (%)	EL <sub>max</sub> (nm)	FWHM <sup>d</sup> (nm)	CIE <sup>e</sup> (x,y)
o-TP-EPY	8.8	0.41	0.16	1.27	419	43	(0.175, 0.068)
m-TP-EPY	8.2	2.13	0.90	4.61	440	47	(0.157, 0.079)
p-TP-EPY	8.7	0.59	0.24	1.88	423	42	(0.173, 0.063)

<sup>a</sup> Luminescence efficiency.

<sup>b</sup> Power efficiency.

<sup>c</sup> External quantum efficiency.

<sup>d</sup> FWHM (full width half maximum).

<sup>e</sup> 1931 Commission Internationale de l'Eclairage/NTSC (National Television System Committee): CIE (0.14, 0.08).



**Fig. 4.** EL spectra of *o*-TP-EPY ( $\blacksquare$ ), *m*-TP-EPY ( $\bigcirc$ ), and *p*-TP-EPY ( $\blacktriangle$ ) in OLED devices. The inset shows the CIE (*x*, *y*) coordinates of the *o*-, *m*-, and *p*-TP-EPY devices.

was 4.61%, which is 3.6 and 2.4 times the values for *o*-TP-EPY (1.27%) and *p*-TP-EPY (1.88%), respectively. This difference can be explained by the following two factors. First, *m*-TP-EPY has a higher PL quantum yield (73%) compared to *o*-TP-EPY (42%) and *p*-TP-EPY (61%). Second, *o*-TP-EPY and *p*-TP-EPY exhibit wider band gaps (3.11 and 3.08 eV) than *m*-TP-EPY (2.87 eV), making carrier injection difficult in OLED devices based on *o*-TP-EPY and *p*-TP-EPY. These factors caused the EL efficiency of *o*-TP-EPY and *p*-TP-EPY to be lower than that of *m*-TP-EPY. The EQE for *p*-TP-EPY, 1.88%, is superb; the excellent violet emitting materials presented previously, F<sub>2</sub>PA and CBP, have EQE values of 1.95% and 1.25%, respectively [36,37].

# 4. Conclusions

New indenopyrazine derivatives with bulky *m*-terphenyl side groups substituted at the *ortho*, *meta*, or *para* junction positions were successfully synthesized. There are larger blue shifts in the *Abs* and PL spectra of *o*-TP-EPY and *p*-TP-EPY than in those of *m*-TP-EPY for both the solution and thin-film states, resulting in violet PL emission. These findings are consistent with the results of our molecular calculations, which indicate that the side group position on the indenopyrazine core, in particular whether the side group coincides with a node or lobe in the orbital structure, affects the  $\pi$ -conjugation of the molecule and hence alters the optical properties. These changes in optical properties are reflected in the behavior of the nondoped OLED devices fabricated using the synthesized compounds. In particular, the device containing *p*-TP-EPY (high  $T_{\rm g}$ , 127 °C) was found to exhibit excellent properties: an EL spectrum with a peak at 423 nm for violet emission at CIE coordinates (0.173, 0.063) and an EQE of 1.88%.

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