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Highly twisted pyrene derivatives for non-doped blue OLEDs

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Abstract:

New highly twisted rigid blue light-emitting materials were designed, composed of pyrene with a xylene core unit and either naphthalene or phenyl end units. These blue-emitting materials were synthesized via the Suzuki cross-coupling reaction and their structures were confirmed using FT-IR, ¹H NMR, ¹³C NMR, and mass spectroscopy. The optical, electrochemical and thermal properties of the materials were investigated. The non-coplanar structure introduced by highly twisted xylene units provides steric hindrance, resulting in very deep blue emission. The fabricated devices exhibited a maximum external quantum efficiency (EQE) of 3.69% with CIE color coordinates (x, y: 0.15, 0.06).

Keywords: blue, fluorescence, OLED, pyrene, xylene

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted considerable attention or their emission properties at wide viewing angle angles and their application to flat-panel displays [1-6]. Blue, green and red emitters with have high emission efficiency and high color purity are required for full color display applications. Green and red emitters are usually used in phosphorescent systems, while blue emitters are still used in fluorescent systems, so developing effective blue OLEDs is an important part of developing these systems. The color purity of blue emitters can affect power consumption and is an important issue for researchers [7-11]. It is very difficult to develop color pure and efficient blue emitters due to the wide band gap required, regardless of the type of material.

Research has revealed that host-guest systems experience some problems such as phase separation upon heating, complexity due to addition of dopants, and the high cost of mass production, despite improved EL efficiency [12-13]. Non-doped emitting layer systems may therefore have advantages over host-guest systems.

Pyrene has strong π electron delocalization energy and efficient fluorescence properties due to its large planar conjugated aromatic characteristics [14]. Some pyrene derivatives have been used in OLEDs to improve hole transport through their electron-rich characterization [15].

Recently, our group reported anthracene derivatives with a xylene group, with highly twisted and rigid non-planar structures, which prevents the close-packing of molecules in the solid state and increases efficiency through reduced vibronic coupling. These anthracene derivatives exhibited high efficiency and color- pure blue emission [11, 16].

In this study, we designed and developed new pyrene derivatives containing xylene units, specially, 1,6-bis(2,5-dimethyl-4-naphthalene-2-yl)phenyl)pyrene (BDNP) and 1,6-bis(2,5-dimethyl-4-phenyl)phenyl)pyrene (BDPP). BDNP and BDPP which have bulky, rigid non-coplanar structures due to steric tortional hindrance of the 2,5-dimethyl phenyl (xylene) unit, are expected to demonstrate efficient and color-pure blue emission.

2. Experimental Section

2.1. Materials

All starting materials were purchased from Aldrich and TCI. Pd catalyst was purchased from Umicore. All starting materials were used without further purification. 3,4-Dibromothiophene-1,1-dioxide and 2,3-dibromoanthraquinone were prepared according to literature procedures [17]. All solvents were further purified prior to use.

2.2. Instruments

¹H NMR spectra were recorded using a Bruker Avance 300 MHzFT NMR spectrometer, and chemical shifts (ppm) were reported with tetramethylsilane (TMS) as an internal standard. Fourier transform (FT)-IR spectra were recorded using a Shimadazu FT-IR spectrometer. Thermogravimetric analysis (TGA) was carried out on a TA instruments 2100 TGA analyzer under nitrogen atmosphere at a rate of 10°C/min. Differential scanning calorimeter (DSC) was performed using a TA DSC 2010 device under nitrogen atmosphere at a rate of 10 °C /min. Melting points was determined using an Electrothermal digital melting point IA 9000 analyzer. UV–vis absorption spectra were measured using a Shimadsu UV-1065PCUV–vis spectrophotometer. The photoluminescence (PL) spectra were measured by Perkin-Elmer LS50B fluorescence spectro meter. The electrochemical properties of the materials were measured by cyclic voltammetry (CV) using Epsilon C3 in 0.1 M solution of tetrabutyl ammonium perchlorate (TBAP) in chloroform.

2.3. Synthesis

2.3.1 Synthesis of 2-naphthalene boronic acid

In the THF (300 mL) and 2-bromonaphthalene (30 g, 0.03 mmol) at -78 C, 2.5 M nbutyllithium (69.54 mL, 0.17 mmol) was slowly added. After 1 h stirring, triethyl borate (31.7 g, 0.22 mmol) was added at -78 °C. The mixture was stirred for 3 h, and the mixture was extracted with ethyl acetate and water. After the crude product was dried by MgSO₄ the solvent was evaporated. The product was purified by hexane. Yield: 21.8 g (87%); ¹H NMR (CDCl₃, 300MHz, ppm): $\delta = 8.37$ (s, 1H), 8.18 (s, 2H), 7.95-7.83 (m, 4H), 7.55-7.48 (m, 2H).

2.3.2 Synthesis of (1-bromo-2,5-dimethyl-4-phenyl)benzene

The mixture of 1,4-dibromo-2,5-dimethylbenzene (40 g, 151.54 mmol), phenyl boronic acid (14.8 g, 121. 23 mmol), 2M K₂CO₃ (120 mL), and tetrahydrofuran (400 mL) was degassed. After Pd(PPh₃)₄ (7.22 g, 4.55 mmol) was added in the mixture, it was stirred for 24 h at 90 °C. The mixture was extracted with methylene dichloride and water. The crude product was purified by column chromatography using hexane. Yield: 23.2 g (36.7 %); ¹H NMR (CDCl₃, 300MHz, ppm): δ = 7.57 (s, 1H), 7.56-7.45(m, 4H), 7.37-7.33 (dd, 1H), 7.25 (s, 1H), 2.44 (s, 3H), 2.27 (s, 3H).

2.3.3 Synthesis of (1-bromo-2,5-dimethyl-4-naphthyl)benzene

The reaction was similarly proceeded as synthesis of 1-bromo-2,5-dimethyl-4-phenyl benzene.

Yield: 25.5 g, 72%; ¹H NMR (CDCl₃, 300MHz, ppm): δ = 7.93-7.87 (m, 3H), 7.77 (s, 1H), 7.58-7.51(m, 3H), 7.47-7.43 (dd, 1H), 7.22 (s, 1H), 2.44 (s, 3H), 2.27 (s, 3H).

2.3.4 Synthesis of (2,5-dimethyl-4-phenyl)phenyl boronic acid

In the THF (300 mL) and (1-bromo-2,5-dimethyl-4-phenyl)benzene (5 g, 19.1 mmol) at -78 $^{\circ}$ C, 2.5 M n-butyllithium (8.42 mL, 21.06 mmol) was slowly added. After 1 h stirring, triethyl borate (3.07 g, 21.06 mmol) was added at -78 $^{\circ}$ C. The mixture was stirred for 8 h, and the mixture was extracted with ethyl acetate and water. After the crude product was dried by MgSO₄ the solvent was evaporated. The product was purified by hexane. Yield: 2.87 g (66.3%); ¹H NMR (DMSO, 300MHz, ppm): δ =8.022 (s, 2H), 7.43(m, 2H), 7.36(m, 4H), 6.95 (s, 1H), 2.37 (s, 3H), 2.17 (s, 3H).

2.3.5 Synthesis of (2,5-dimethyl-4-(2'-naphthyl)phenyl boronic acid

The synthesis was proceeded by same synthetic method of (2,5-dimethyl-4-phenyl)phenyl boronic acid. Yield: 23.2 g, 86.3%; ¹H NMR (300 MHz, CDCl₃, ppm): δ =8.10 (s, 2H), 7.97 (m, 3H), 7.86 (s, 1H), 7.55 (m, 3H), 7.29 (s, 1H), 7.19 (s, 1H), 2.28 (s, 3H), 2.26 (s, 3H).

2.3.6 Synthesis of 1,6-bis(2,5-dimethyl-4-phenyl)phenyl)pyrene (BDPP)

1,6-Dibromopyrene (2g, 4.95 mmol), (2,5-dimethyl-4-phenyl)phenyl boronic acid (2.8 g, 12.38 mmol), 2M NaOH (8mL) and THF (100 mL) were mixed. Pd(PPh₃)₄ (0.20 g, 0.12 mmol) was added to the mixture, and it was stirred for 24 h at 90 °C. The mixture was added to ethanol, and the crude solid was filtered. The product was purified by soxhlet using chloroform. Yield: 2.03 g, 72.8 %; ¹H NMR (300 MHz, CD₂Cl₂, ppm): δ = 8.25 (2H, d), 7.93 (2H, s), 8.08 (2H, d), 7.96 (2H, d), 7.88 (4H, d), 7.52-7.50 (8H, m), 7.33-7.32 (6H, s), 2.37 (6H, s), 2.09 (6H, s). HRMS (EI+): m/z calcd for (C₄₄H₃₄)562.2661; found 562.2664.

2.3.7 Synthesis of 1,6-bis(2,5-dimethyl-4-naphthyl)phenyl)pyrene (BDNP)

The synthesis was proceeded by same synthetic method of 1,6-bis(2,5-dimethyl-4-phenyl)phenyl)pyrene (BDNP). Yield: 4.9 g, 88.7 %; ¹H NMR (300 MHz, CDCl₃, ppm): $\delta = 8.29$ (2H, d), 8.12 (2H, d) 8.09 (12H, m), 7.69 (2H, dd), 7.58-7.55 (4H, m), 7.41 (2H, s), 2.42 (6H, s), 2.13 (6H, s). HRMS (EI+): m/z calcd for (C₅₂H₃₈) 662.2974; found 662.2976.

2.4. OLEDs device fabrication and measurement

ITO was cleaned by the standard oxygen plasma treatment. The OLED grade materials except BDPP and BDNP were purchased and used with-out further purification. All organic layers were deposited in a high vacuum chamber below 6.67×10^{-5} Pa and thin films of LiF and Al were deposited as a cathode electrode by a thermal evaporation method. The OLEDs were transferred directly from vacuum into an inert environment glove-box, where they were encapsulated using a UV-curable epoxy, and a glass cap with a moisture getter. The electroluminescence spectrum and current density-voltage-luminescence (*J-V-L*) were

measured using a Minolta CS-2000 and a current/voltage source/measure unit (Keithley 238) [18].

3. Results and discussion

3.1. Synthesis and characterization

Synthetic scheme for the two pyrene derivatives, BDNP and BDPP, are shown in Scheme 1. BDNP and BDPP were synthesized using a simple twofold by two times Suzuki coupling reaction. Phenyl boronic acid and naphthyl boronic acid were reacted with 1,4-dibromo-2,5dimethylbenzene to give 1-bromo-2,5-dimethyl-4-phenylbenzene and 1-bromo-2,5-dimethyl-4-naphthylbenzene, respectively. The Suzuki coupling reaction was employed between monobromide and pyrene boronic ester to obtain the target compounds. The molecular structures of BDNP and BDPP were fully characterized using ¹H-NMR and high resolution mass spectrometry

3.2. Computational investigations

To improve EL performance, highly twisted pyrene derivatives with xylene groups were designed. Computer simulations using density function theory (DFT) were performed to optimize the structures, using the B3LYP/6-31G* method in Gaussian 03. The optimized molecular structures of BDNP and BDPP are shown in Fig. 1. The electron densities of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of both BDNP and BDPP were delocalized on the pyrene core regardless of whether they contained phenyl or naphthyl end groups; this may be due to the steric

hindrance of the xylene units resulting in a highly twisted structure. This structure improves the color purity because intermolecular interaction is disrupted and recrystallization is suppressed.

3.3. Thermal properties

Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) of measurements for BDPP and BDNP are shown in Fig. 2. In the DSC spectra of heating (10 °C/min), the two materials have no obvious glass transition. In addition, no crystallization processes were observed in the DSC trace. These results imply that the bulk structures of BDNP and BDPP are morphological stable. Both BDPP and BDNP were thermally stable up to 447 °C. These results show that these materials are amorphous with good thermal stability, desirable characteristics for OLED performance.

3.4. Optical properties

The solution and film state UV absorption and PL spectra of BDNP and BDPP are shown in Fig. 3. Absorption maxima of BDPP in solution state were observed at 284, 338, and 352 nm, and in the film state at 287, 343, and 358 nm. For BDNP, absorption maxima in solution were observed at 283, 338, and 351 nm and in the film state at 286, 342, and 359 nm. Although a small bathochromic shift occurred in the film state, both BDNP and BDPP exhibited similar UV-absorption properties. The results suggest that both BDNP and BDPP are highly twisted structures regardless of whether they contain phenyl or naphthyl side groups, and that extended conjugation to side groups is inhibited because of the steric stain of the xylene

group. The absorption maxima of both BDPP and BDNP were 40-50 nm blue shifted compared to anthracene core with phenyl or naphthyl end capped xylene groups.

The fluorescence spectra in solution revealed feature bands at 386 and 403 nm for BDPP and at 399 nm for BDNP. Fluorescence spectra for thin film revealed bands at 381, 402 and 426 nm for BDPP and at 404 and 425 nm for BDPP. Both BDPP and BDNP exhibited similar deep blue emission even in the film state.

3.5. Electrochemical properties

The electrochemical characteristics of BDNP and BDPP were investigated using cyclic voltammetry and measuring the optical band gap from the absorption edge. The HOMO, LUMO, and band gap values for BDNP and BDPP are summarized in Table 1. BDNP and BDPP both exhibited wide optical energy gaps (E_g) of 3.06 and 3.16 eV, respectively, and are expected to be suitable candidates for deep blue emitters.

3.6. Electroluminescence properties

Figure 4 shows the structures of blue OLEDs fabricated in this study using non-doped BDNP or BDPP. The detailed structure of Device A was as follows: indium tin oxide (ITO)/N,N'-di(naphthalene-1-yl)-N,N'-diphenylbenzidine (NPB) (50 nm)/BDPP (40 nm)/1,3-bis(3,5-di-pyrid-3-yl-phenyl)benzene (BmPyPB) (10 nm)/LiF/Al, where NPB is the hole transporting layer (HTL); BDPP is the blue emitting layer (EML); BmPyPB is the electron transporting layer (ETL), and LiF is the electron injection layer (EIL) at the Al cathode interface [17-19]. Devices B had an identical structure, except that BDNP was used for the EML material instead of BDPP. Figure 5 shows the current–luminance–voltage

characteristics of the fabricated devices. Both devices exhibited low turn-on voltages of 4.0 V at 10 cd m^2 .

Figure 6 shows the normalized EL spectra of the fabricated devices. The spectra revealed deep blue emissions with peaks at 436 (BDPP), and 440 nm (BDNP). Moreover, both BDPP and BDNP exhibited a narrow full-width at half-maximum (FWHMs) of about 50 nm without excimer or exciplex emission. This small value can be explained by the highly twisted structure of BDPP and BDNP due to dimethyl groups containing a xylene group, which results in steric hindrance toward the pyrene unit and the end group [20-21]. Hence, close-packing is inhibited in the synthesized molecules. The CIE coordinates of Devices A (DBPP), and Device B (BDNP) were (0.15, 0.06), and (0.16, 0.06), respectively, at a luminance of 1000 cd/m^2 .

The external quantum efficiency (EQE) and current efficiency (CE) vs. current density characteristics of the fabricated blue OLEDs are plotted shown in Fig. 7. Both devices exhibited good light-emitting performance, and in particular, Device A containing BDPP EML material exhibited a maximum EQE of 3.69% and CE of 2.03 cd/A. Key device performance parameters and EL emission characteristics are summarized in Table 2.

4. Conclusions

We designed and developed new deep blue light-emitting materials composed of a pyrene core with highly twisted xylene units. The non-coplanar structure due to steric hindrance of the introduced substituent resulted in very deep blue emissions with a maximum EL peak of 436 nm and narrow FWHM of 50 nm. In particular, the device using BDPP exhibited a peak EQE of 3.69% with CIE color coordinates (x, y: 0.15, 0.06).

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Scheme 1. Synthesis of 1,6-Bis(2,5-dimethyl-4-phenyl)phenyl)pyrene (BDPP) and 1,6-Bis(2,5-dimethyl-4-naphthyl)phenyl)pyrene (BDNP)

Table Caption

Table 1 Physical properties of BDPP and BDNP.

Table 2 OLED device characteristics using BDPP and BDNP as non-doped and doped blue emitters

Figure Captions

Fig. 1 Calculated stereostructure and frontier orbital of BDPP (left) and BDNP (right).

Fig. 2 TGA thermogram and DSC thermogram of (a) BDPP and (b) BDNP at a heating rate of 10 °C/min.

Fig. 3 UV-vis absorption and photoluminescence emission spectra of (a) BDPP and (b) BDNP.

Fig. 4 Energy diagrams of devices using BDPP and BDNP as a non-doped emitter.

Fig. 5 Current density–voltage–luminance (*J-V-L*) characteristics of the fabricated blue OLEDs.

Fig. 6 Normalized EL spectra of the devices using BDPP and BDNP as a non-doped emitter.

Fig. 7 (a) External quantum and (b) current efficiency vs. current density characteristics of the fabricated blue OLEDs.

Scheme 1. Synthesis of 1,6-Bis(2,5-dimethyl-4-phenyl)phenyl)pyrene (BDPP) and 1,6-Bis(2,5-dimethyl-4-naphthyl)phenyl)pyrene (BDNP)



	UV sol (nm)	UV film (nm)	PL sol (nm)	PL film (nm)	Td (°C)	Tg (°C)	Tm (°C)	HOMO (eV)	LUMO (eV)	Band gap (eV)
BDPP	273, 284, 338, 352	272, 287, 343, 358	386, 403	381, 402, 426	372	-	-	5.85	2.69	3.16
PBNP	283, 338, 351	286, 342, 359	392	425	446	-	-	5.59	2.53	3.06

Table 1 Physical properties of BDPP and BDNP.

Table 2 OLED device characteristics using BDPP and BDNP as non-doped and doped blue emitters

Device	CE _{max} [cd/A]	EQE _{max} [%]	EL _{max} [nm]	CIE [x, y]
A (BDPP)	2.03	3.69	436	(0.15, 0.06)
B (BDNP)	1.88	3.15	440	(0.16, 0.06)

Device structure A: ITO / NPB (50 nm) / BDPP (40 nm) / BmPyPB (10 nm) / LiF (0.5 nm) / Al (70nm)

Device structure B: ITO / NPB (50 nm) / BDNP (40 nm) / BmPyPB (10 nm) / LiF (0.5 nm) / Al (70nm)



Fig.1 Calculated stereostructure and frontier orbital of BDPP (left) and BDNP (right)

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Fig. 7 (a) External quantum and (b) current efficiency vs. current density characteristics of the fabricated blue OLEDs.



Research highlights

▶ Deep blue emitting materials based on pyrene core ▶ Highly twisted blue emitting materials by xylene units ▶ 3-Dimensionally highly twisted non-coplanar ▶ Non-doped device using new pyrene exhibited efficiency of 3.69%. ▶ Non-doped EL devices showed high color purity of (0.15, 0.06).

Keywords: Blue OLED; limb structure; anthracene derivatives; quantum efficiency; color purity; non-coplanar structure