



Journal of Nanoscience and Nanotechnology Vol. 16, 8796-8799, 2016 www.aspbs.com/jnn

# Synthesis and Physical Properties of New Pyrene **Derivative with Bulky Side Groups for Blue Emission**

Mina Jung, Jaehyun Lee, Hyocheol Jung, and Jongwook Park\*

Department of Chemistry/Display Research Center, The Catholic University of Korea, Bucheon, 420-743, Korea

Organic light-emitting diodes (OLEDs) have attracted much attention from academia and industry field because of their various applications such as large area flat-panel displays and lightings. We designed and synthesized new pyrene derivative with 1,6-bis(3',5'-diphenylbiphenyl-4-yl)pyrene (1,6-DTBP) which has bulky side group for intra-twisted structure and blue emission. In solution state, 1,6-DTBP exhibited absorption maximum value of 365 nm and photoluminescence (PL) maximum value of 425 nm. In film state, 1,6-DTBP exhibited absorption maximum value of 373 nm and PL maximum value of 461 nm without excimer band. 1,6-DTBP can be applicable to OLED emitter as a blue emission.

Keywords: OLEDs, Pyrene, Blue Fluorescent Emitter, Core-Side Concept.

## **1. INTRODUCTION**

IP: 46.161.56.174 On: Thu 26 Apr 2018 (CIE<sub>x,y</sub>) coordinate (0.156, 0.088) than Organic light-emitting diodes (OLEDs)<sup>1-5</sup> based on small organic molecules are under many intense researches in view of their promising future for large full color display applications such as TV and advertising displays. OLED has been under active researches so far with its overlooking high potential for use in liquid crystal display (LCD) backlight and lighting field due to its low power consumption.6,7

At the heart of full color display is the development of stable and highly efficient red, green, and blue (RGB) emitting materials.8 Among the red, green and blue emitting materials used in OLED, blue ones are characterized especially as low efficiency and short device lifetimes because of its wide band gap. Blue light means that it includes high energy band gap as well as a steep energy barrier at the hole and electron injection interfaces inside of device compared to red and green emitter.

In past research, we have reported new high performance blue-light emitters based on anthracene core derivatives using core-side concepts.<sup>9</sup> For example, 9,10-bis(3",5"diphenylbiphenyl-4'-yl)anthracene (TAT) was synthesized using anthracene core group with triphenylbenzene group as bulky side group. This material has better thermal properties, a better luminance efficiency, a higher power efficiency, and a deeper blue Commission Internationale

Among derivatives used diverse core groups like anthracene, pyrene, phenanthrene, and chrysene well known as blue emitting materials, pyrene and its derivatives received the spotlight as they provide high PL quantum efficiency, thermal and chemical stabilities.10 In this work, we designed and synthesized 1,6-bis(3',5'diphenylbiphenyl-4-yl)pyrene (1,6-DTBP) using pyrene core group with triphenylbenzene group as bulky side groups for blue emission (see Scheme 1).

2-methyl-9,10-di(2'-naphthyl)anthracene(MADN).

# 2. EXPERIMENTAL DETAILS

#### 2.1. General Experiment

<sup>1</sup>H-NMR spectra were recorded on Bruker, Advance 300. The optical absorption spectra were obtained by Lambda 1050 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photoluminescence (PL) spectroscopy. HOMO value was measured by RIKEN Surface analyzer AC-2. MALDI TOF-TOF 5800 System was used for mass spectroscopy. OLED device was fabricated as the following structure: ITO/2-TNATA (60 nm)/NPB (15 nm)/EML (35 nm)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (200 nm), where, 4,4',4''-Tris(N-(naphthalen-2-yl)-N-phenylamino) triphenylamine [2-TNATA] as hole injection layer, N, N'-bis(naphthalen-1-y1)-N,N'-bis(phenyl)benzidine [NPB] as hole transport layer, and 8-hydroxyquinoline aluminum [Alq<sub>3</sub>] as

<sup>\*</sup>Author to whom correspondence should be addressed.

<sup>1533-4880/2016/16/8796/004</sup> 



Scheme 1. Chemical structure of the synthesized material.

electron transporting and emission layer, 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<sup>2</sup>, and the Al layer was continuously deposited under the same vacuum condition. *I*–*V*–*L* characteristic of OLED device and EL spectrum were obtained using a Keithley 2400 source measure unit and a Minolta CS-1000A spectrophotometer.

## 2.2. Synthesis of Tetramethyl-3',5'-Diphenylbiphenyl-4-yl-[1,3,2]-Dioxaborolane, (Compound [9])

Compound [8] (3 g, 7.78 mmol) was added to 13 mL of anhydrous THF and stirred at -78 °C under a nitrogen atmosphere, then 2 M *n*-BuLi (5.83 mL, 11,68 mmol) was added to the reaction mixture. Next, isopropoxy-4,4,5,5tetramethyl-1,3,2-dioxaborolane (3.24 mL, 15.6 mmol) was added to the reaction mixture after 30 min. After the reaction was complete, the reaction mixture was extracted with ethyl acetate and water. The organic layer was dried with anhydrous MgSO<sub>4</sub> and filtered. The solvent was removed by evaporation. The product was purified by silica gel column chromatography using THF: *n*-hexane (1:10) (3.03 g, yield 90%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 7.94(*d*, 2H), 7.80(*m*, 3H), 7.73(*m*, 6H), 7.51(*t*, 4H), 7.42(*t*, 2H), 1.24(*d*, 12H).

## 2.3. Synthesis of 1,6-Dibromopyrene (Compound [2])

Bromine (10.0 mL, 195 mmol) in CHCl<sub>3</sub> (500 mL) was dropped into a solution of pyrene (20.0 g, 98.9 mmol) in CHCl<sub>3</sub> (500 mL) over 5 h while stirring. The precipitate was collected after 12 h and resolved by fractional crystallization from xylene (5.01 g, yield 14.07%). <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 8.49(*d*, 2H), 8.29(*d*, 2H), 8.15(*d*, 2H), 8.08(*d*, 2H).

### 2.4. Synthesis of 1,6-Bis(3',5'-Diphenylbiphenyl-4-yl) Pyrene (1,6-DTBP)

Compound [2] (1 g, 2.76 mmol), compound [9] (2.63 g, 6.08 mmol) and  $Pd(OAc)_2$  (0.23 g, 0.52 mmol) were added to 30 mL of anhydrous THF and anhydrous toluene 170 mL mixture. Then tetraethylammonium hydroxide (20 wt%) (35 mL) was added to the reaction mixture at

J. Nanosci. Nanotechnol. 16, 8796-8799, 2016

50 °C. The mixture was heated to 80 °C for 2 h under nitrogen. After the reaction was complete, the reaction mixture was filtered. The product was isolated using silica gel column chromatography with CHCl<sub>3</sub> as the solvent. The eluent was removed by evaporation. Recrystallization of the residue from CHCl<sub>3</sub> afforded a solid product (0.16 g, yield 6.92%). <sup>1</sup>H-NMR (300 MHz, THF)  $\delta$ (ppm): 8.33(*m*, 4H), 8.16(*d*, 2H), 8.07(*d*, 2H), 8.05(*m*, 8H), 7.93(*s*, 2H), 7.86(*m*, 12H), 7.52(*t*, 8H), 7.41(*t*, 4H). TOF-MS 810.3 m/z.

## 3. RESULTS AND DISCUSSION

The synthesis routes to the 1,6-DTBP are shown in Scheme 2. In blue emitting material, it has generally core and side moieties. 1,6-DTBP introduced pyrene as the core group with high PL quantum yield of 0.65% which is two times higher than that of anthracene. However, the use of pyrene as efficient emitters in OLED has been limited, because the planar structure of pyrene has strong tendency to form excimers in the solid state, which results in long-wavelength excimers emission with low fluorescence quantum yield and emission quenching.<sup>11</sup> In order to prevent this limitation, bulky triphenylbenzene group was introduced as the side group to pyrene core.

UV-Visible (UV-Vis.) absorption and PL spectra of the synthesized compound in the THF solution and the u, 26 Apr 2018 07:57:57



Scheme 2. Synthetic routes of 1,6-DTBP.

8797



**Figure 1.** UV-Visible absorption and PL spectra of 1.6-DTBP: (a) solution state in THF  $(1.0 \times 10^{-5} \text{ M})$ , (b) evaporated film state.

evaporated film state were measured as shown in Figure 1 and Table I. In the THF solution state, 1,6-DTBP exhibits a absorption maximum ( $UV_{max}$ ) value of 365 nm and PL maximum ( $PL_{max}$ ) value of 425 nm. In film state, 1,6-DTBP showed  $UV_{max}$  of 373 nm and  $PL_{max}$  of 461 nm. In PL spectrum of film state, excimer emission was not exhibited. In comparison to solution state,  $UV_{max}$  and  $PL_{max}$  of film state were respectively red-shifted by 8 nm and 36 nm, which indicated an increase in conjugation length in the solid state.<sup>12</sup> The increase in conjugation length might be due to the conformation of solid state  $\pi$ -stacked compounds being more planar. Furthermore, the full widths at half maximum (FWHM) of 1,6-DTBP was found to be 54 nm in solution state and 68 nm in film state.

The molecular structure of 1,6-DTBP was optimized by using density functional theory (DFT) calculated at

Table I. Optical properties of 1,6-DTBP.

	Solution <sup>a</sup>			Film <sup>b</sup>		
	UV <sub>max</sub> (nm)	PL <sub>max</sub> (nm)	FW HM (nm)	UV <sub>max</sub> (nm)	PL <sub>max</sub> (nm)	FW HM (nm)
1,6-DTBP	365	425	54	373	461	68

Notes: <sup>a</sup>: Solution state of THF  $(1 \times 10^{-5} \text{ M})$ , <sup>b</sup>: Film state.

Figure 2. Electron density distributions of HOMO and LUMO in the 1,6-DTBP calculated with B3LYP/6-31G.

the B3LYP/6-31G level as shown in Figure 2. In the optimized structure, 1,6-DTBP has highly twisted coreside angle of 90.1° between the pyrene and triphenylbenzene group. Highly twisted structure can prevent excimer in film state by effectively reducing intermolecular  $\pi - \pi$ interaction. Therefore, there is no excimer band at PL spectrum.

Highest occupied molecular orbital (HOMO) value for the 1,6-DTBP was measured by AC-2 at -5.70 eV. Optical band gap of 2.94 eV was calculated from the UV-Vis. absorption spectrum.

Lowest unoccupied molecular orbital (LUMO) value of -2.76 eV calculated from the HOMO and optical band gap. Those data are summarized in Table II.

The device structure was fabricated as ITO/2-TNATA (60 nm)/NPB (15 nm)/EML (35 nm)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (200 nm). I-V-L curve was shown in Figure 3. OLED device based on 1,6-DTBP exhibited luminance efficiency of 4.19 cd/A. Power efficiency was 1.87 lm/W. The EL maximum value of 1,6-DTBP was exhibited at 468 nm of blue emission (Fig. 3). In case of CIE value, 1,6-DTBP was shown at (0.16, 0.19).

Table II. Electrochemical property of 1,6-DTBP.

	$HOMO^{a}$ (eV)	$LUMO^{b}$ (eV)	Band gap (eV)
,6-DTBP	-5.70	-2.76	2.94

*Notes*: <sup>*a*</sup>: Ultraviolet photoelectron spectroscopy (Riken-keiki, AC-2), <sup>*b*</sup>: LUMO obtained from the HOMO and the optical band gap.

Jung et al.

Jung et al.



**Figure 3.** (a) *I*–*V*–*L* data of OLED device, (b) EL spectrum of OLED device: ITO/2-TNATA (60 nm)/NPB (15 nm)/EML (35 nm)/Alq<sub>3</sub> (20 nm)/LiF (1 nm)/Al (200 nm).

## 4. CONCLUSION

We designed and synthesized 1,6-DTBP as a new blue emitting material in OLED with pyrene as the core group and triphenylbenzene group as the side group. Triphenylbenzene group is a bulky side group introduced to effectively prevent  $\pi - \pi$  interaction of pyrene and excimer in film state. 1,6-DTBP in solution state showed UV<sub>max</sub> of 365 nm and PL<sub>max</sub> of 425 nm. In film state, they were 373 nm and 461 nm, respectively. OLED device based on 1,6-DTBP exhibited luminance efficiency of 4.19 cd/A. Power efficiency was 1.87 lm/W.

**Acknowledgments:** This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Trade, Industry and Energy, Republic of Korea (Project No. 10050215).

#### **References and Notes**

- H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C. Adachi, *Nature* 492, 234 (2012).
- Z. S. H. Park, J. E. Kwon, and S. Y. Park, J. Am. Chem. Soc. 131, 14043 (2009).
- J. S. Kim, J. Heo, P. Kang, J. H. Kim, S. O. Jung, and S. K. Kwon, Macromol. Res. 17, 91 (2009).
- Y. S. Choe, S. Y. Park, D. W. Park, and W. H. Kim, *Macromol. Res.* 14, 38 (2006).
- H. T. Park, D. C. Shin, S. C. Shin, J. H. Kim, S. K. Kwon, and Y. H. Kim, *Macromol. Res.* 19, 965 (2011).
- 6. L. Ruppel, S. Mogck, and C. May, IWFPE 2009 (2009), Invited 6.1.
- W. Y. Lai, J. Levell, A. Jackson, S. C. Lo, P. Bernhardt, I. W. Samuel, and P. Burn, *Macromolecules* 43, 6986 (2010).
- 8. Y. I. Park, J. H. Son, J. S. Kang, S. K. Kim, J. H. Lee, and J. W. Park, *Chem. Commun.* 18, 2143 (2008).

9. S. K. Kim, B. Yang, Y. Ma, J. H. Lee, and J. W. Park, J. Mater. Chem. 18, 3376 (2008).

- F. Liu, C. Tang, Q. Q. Chen, F. F. Shi, H. B. Wu, L. H. Xie, B. Peng, W. Wei, Y. Cao, and W. Huang, *J. Phys. Chem. C* 113, 4641 (2009).
- 11. M. Ottonelli, M. Piccardo, D. Duce, S. Thea, and G. Dellepiane, J. Phys. Chem. A 116, 611 (2012).
- 12. D. Vak, B. Lim, S. H. Lee, and D. Y. Kim, Org. Lett. 7, 4229 (2005).

Received: 20 May 2015. Accepted: 12 August 2015.