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Synthesis and Property of New Blue Emitting Materials with Bulky Side Group

SEOKWOO KANG, HAYOON LEE, BEOMJIN KIM, HYEONMI KANG, AND JONGWOOK PARK*

Department of Chemistry, The Catholic University of Korea, Bucheon, Korea

Two emitting compounds, 9,10-bis-[1,1';3',1"]terphenyl-5'-yl-1,5-di-o-tolyl-anthra cene [TP-DTA-TP] and 9,10-bis-phenyl[1,1';3',1"]triphenyl-5'-yl-1,5-di-o-tolylanthracene [TPB-DTA-TPB] based on new twisted core moiety were synthesized through boration, Suzuki reaction, and Sandmeyer reactions. EL performance was improved by varying the chemical structure of the side group. Physical properties such as optical, electrochemical, and electroluminescent properties were investigated. Synthesized compounds were used as an EML in OLED device: ITO / 2-TNATA (60nm) / NPB (15nm)/ TP-DTA-TP or TPB-DTA-TPB (35 nm) / Alq3 (20nm) / LiF (1nm) / Al (200nm). It was found that TPB-DTA-TPB showed higher luminance efficiency and better C.I.E. value than TP-DTA-TP device.

Keywords OLEDs; Blue materials; Bulky Side group; Anthracene

Introduction

Since electroluminescence (EL) result in small molecular organic materials (Tang et al.) was announced in 1987, studies on organic semiconductors such as organic light emitting diodes (OLED) [1–3], organic thin film transistors (OTFT) [4] and organic photovoltaics (OPVs) have been actively conducted [5]. Many efforts have been made in recent years to improve the performance and stability of OLEDs because of their potential application in flat panel displays [6–11]. In order to make full color OLED display, we need high performance red, green and blue materials with high EL efficiency, pure color coordinate (C.I.E.) value and long life time, as well as material thermal property. Host and dopant methods in fluorescence and phosphorescence systems have been used to get efficiency of OLED, and red and green emitters have been developed and improved to commercialize full color OLED. However, there are many problems to be solved, such as blue emitting material, device lifetime and luminous efficiency, etc. Many kinds of blue materials including diarylanthracene, di(styryl)arylene, fluorene and pyrene have been intensively used and studied on improved EL property [12]. The recent research of Pei et al. has shown that spirotruxene derivatives have excellent color coordinates (0.16, 0.09) but maximum external quantum efficiency (EQE) of only 2.9% [13]. Shu et al. have reported anthracene

^{*}Address correspondence to Jongwook Park, Department of Chemistry, The Catholic University of Korea, 43-1, Yeokgok, Wonmi, Bucheon, Korea(ROK). E-mail: hahapark@catholic.ac.kr

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derivatives with color coordinates of (0.14, 0.12) and maximum EQE of 5.3% [14]. Jenekhe et al. have described oligoquinoline derivatives with high EQE of 6.56%, which at the time was the highest reported value for a non-doped blue-light emitter. Unfortunately, however, the color coordinates of this material are (0.15, 0.16), with the value on y-axis larger than 0.1 [15].

In recent papers, we have reported new high performance blue-light emitters based on tetraphenylethylene- and anthracene-cored derivatives [16–18]. Of these synthesized compounds, 9,10-bis(4-(1,2,2-triphenylvinyl)phenyl)anthracene [BTPPA] has a structure with mixed anthracene and tetraphenylene units, which are non-alkylated bulky side groups. This compound has better thermal properties, better luminance efficiency, lower operating voltage, higher power efficiency, and deeper blue CIE x,y coordinates (0.159, 0.135) than other tetraphenylethylene derivatives. The EL performance of these synthesized blue-light emitters can be optimized and improved by varying the chemical structures of the side groups.

Based on these results, we designed new blue-light emitters. First, anthracene moiety with high photoluminescence quantum efficiency was introduced at the center of molecular structure. Second, bulky aromatic rings were attached to anthracene 9, 10-position to improve color properties. Lastly, bulky aromatic rings, m-terphenyl and triphenylbenzene, were used instead of alky groups that induce red-shift of PL and EL and increase in operating voltage. Meta-positioned aromatic ring with short conjugation length was used. This has an advantage of reducing y CIE coordinate value of the emitter [19].

The synthesized compounds are expected to exhibit better than those in our previous studies.

Experimental

Measurements

The ¹H NMR spectra were recorded on Bruker Avance 300. The FAB⁺ mass were recorded on JMS-AX505 WA. 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-luminescence (PL) spectroscopy. Thermal degradation temperature (T_d) of the compounds were measured by thermo-gravimetric analysis (TGA) using SDP-TGA2960 (TA instrument). The current–voltage-luminance (I-V-L) characteristics of the fabricated EL devices were obtained by Keithley 2400 electrometer, and light intensity was obtained by Minolta CS-1000A.

Synthesis

Synthesis of 1,5-dibromoanthraquinone (1). 1,5-Diaminoanthraquinone (10.0 g, 42.0 mmol) and CuBr₂ (21.2 g, 94.6 mmol) were suspended in CH₃CN (200 mL). Tert-butyl nitrite (12.5 mL, 90%) was added under vigorous stirring and the mixture was heated to 65° C for 2.5 h. The mixture was cooled to room temperature (rt), and hydrochloric acid (3 M, 100 mL) and H₂O (100 mL) were added. The solid was filtered after stirring the mixture for additional 20 min, washed with water (4 × 100mL) and EtOH (50 mL), and dried in vacuum. Subsequent filtration of the material through a plug of silica gel using

CHCl₃ as eluent and drying in vacuum yielded 13.7 g of 1,5-dibromoanthraquinone as an orange powder. (88% yield)

¹H-NMR (300MHz, CDCl₃) δ(ppm) : 8.31(dd, 2H), 8.01(dd, 2H), 7.58(t, 2H)

Synthesis of 1,5-dibromoanthracene (2)

10 g (27.1 mmol) of 1,5-bromoanthraquinone was added in a 3-neck round flask, and 400 mL of acetic acid, 50 mL of agitate hydrogen bromide and 82 mL of hypophosphorous acid were sequentially added. The solution was stirred for 4 days at 120° C. After the reaction ended, the solvent was removed by distillation. Subsequent filtration of the material through a plug of silica gel using CHCl₃ as eluent and drying in vacuum yielded 4.2 g of 1,5-dibromoanthracene as a yellow powder. (46% yield)

¹H-NMR (300MHz, CDCl₃) δ(ppm) : 8.82(s, 2H), 8.07(dd, 2H), 7.84(dd, 2H), 7.36(dd, 2H), 2H),

Synthesis of 1,5-di-o-tolyl-anthracene (3). 0.2 g (0.59 mmol) of 1,5-dibromoanthracene, 0.18 g (1.36 mmol) of 2-methylphenylboronic acid and 0.07 g (0.059 mmol) of tetrakis(triphenylphosphine)palladium(0) were added in a 3-neck round flask, and 20 mL of anhydrous toluene was sequentially added. 2mL of 2M NaOH was added. The solution was stirred for 6 hours at 120°C. After the reaction ended, the solution was extracted using chloroform and H₂O. Small amount of H₂O remaining in the chloroform layer was removed using MgSO₄. After obtaining solid by evaporation of product in the chloroform layer, column refinement was performed under chloroform : hexane = 1 : 5 condition. The product obtained by column was dissolved in small amount of chloroform and re-precipitated using methanol before filtering. 0.17 g of white solid was obtained by evaporating the filtered solid. (79% yield)

¹H-NMR (300MHz, THF) δ(ppm) : 8.07(s, 2H), 7.86(d, 2H), 7.45(t, 2H), 7.39-7.23(m, 10H), 2.05 (d, 6H). Fab⁺-MS: 358 m/z

Synthesis of 9,10-dibromo-1,5-di-o-tolyl-anthracene (4). 1.1 g (3.06 mmol) of 1,5-di-otolyl-anthracene was added in a 3-neck round flask, and 100mL of chloroform was sequentially added before slowly adding bromine 0.34 mL (6.75 mmol). The solution was stirred for 6 hours at 50°C. After the reaction ended, the solution was extracted using chloroform and H₂O. Small amount of H₂O remaining in the chloroform layer was removed using MgSO₄. After obtaining solid by evaporation of product in the chloroform layer, column refinement was performed under chloroform : hexane = 1 : 3 condition. The product obtained by column was dissolved in small amount of chloroform and re-precipitated using methanol before filtering. 0.63 g of yellow solid was obtained by evaporating the filtered solid. (40% yield)

¹*H*-*NMR* (300*MHz*, *CDCl*₃) δ(*ppm*) : 8.57-8.56 (*d*, 2*H*), 7.91-7.88(*d*, 2*H*), 7.43-7.25(*m*, 10*H*), 2.05(*d*, 6*H*).

Synthesis of 9,10-Bis-[1,1';3',1''] terphenyl-5'-yl-1,5-di-o-tolyl-anthracene (TP-DTA-TP). 0.7 g (1.35 mmol) of 9,10-dibromo-1,5-di-o-tolyl-anthracene, 1.11 g (3.11 mmol) of 4,4,5,5-tetramethyl-2-[1,1';3',1''] terphenyl-5'-yl-[1,3,2] dioxaborolane and 0.15 g (0.135 mmol) of tetrakis(triphenylphosphine)palladium(0) were added in 3-neck round flask, and 80 mL of anhydrous toluene was added. 10 mL of 2M NaOH was added at 60°C. The solution was stirred overnight. After completion of the reaction, the solution was extracted using chloroform and H₂O. Small amount of H₂O remaining in the chloroform layer was removed using MgSO₄. After obtaining solid by evaporation of product in the chloroform layer, column refinement was performed under chloroform : hexane = 1 : 3 condition. The product obtained by column was dissolved in small amount of chloroform and re-precipitated using methanol before filtering. 0.15 g of yellow solid was obtained by evaporating the filtered solid. (13% yield)

¹H-NMR (300MHz, DMSO) δ (ppm) : 8.44(d, 2H), 7.92-7.79(m, 14H), 7.75-7.73(d, 2H), 7.59-7.48(m, 12H), 7.43-7.41(d, 2H), 7.19-7.13(t, 2H), 7.05-7.01(t, 2H), 6.87-6.79(m, 2H), 6.66-6.59(t, 2H), 2.05(d, 6H). Fab⁺-MS: 814 m/z

Synthesis of 9,10-bis-phenyl[1,1';3',1'']triphenyl-5'-yl-1,5-di-o-tolyl-anthracene (TPB-DTA-TPB)

0.2 g (0.38 mmol) of 9,10-dibromo-1,5-di-o-tolyl-anthracene, 0.36 g (0.85 mmol) of 4,4,5,5-tetramethyl-2-phenyl[1,1';3',1'']triphenyl-5'-yl-[1,3,2]dioxaborolane and 0.05 g (0.038 mmol) of tetrakis(triphenylphosphine)palladium(0) were added in 3-neck round flask, and 30 mL of anhydrous toluene was added. 3 mL of 2M NaOH was added at 60°C. The solution was stirred overnight. After completion of the reaction, the solution was extracted using chloroform and H₂O. Small amount of H₂O remaining in the chloroform layer was removed using MgSO₄. After obtaining solid by evaporation of product in the chloroform layer, column refinement was performed under chloroform : hexane = 1 : 3 condition. The product obtained by column was dissolved in small amount of chloroform and re-precipitated using methanol before filtering. 0.09 g of yellow solid was obtained by evaporating the filtered solid. (24% yield)

¹H-NMR (300MHz, THF) δ (ppm) : 8.64(d, 2H), 8.17(s, 6H), 8.12-8.02(m, 12H), 7.87-7.84(t, 4H), 7.82-7.75(m, 10H), 7.67-7.62(t, 6H), 7.54-7.49(m, 8H), 2.05(dd, 6H). Fab⁺-MS: 966 m/z

Results and Discussion

Scheme 1 shows the chemical structures of the synthesized materials. All compounds were purified with the silica column method, producing pure powders that were characterized by NMR and FAB-MS analysis. The synthesis routes of the compounds are shown in Scheme 1. Boration and Suzuki aryl-aryl coupling reactions were used in overall syntheses. The bulky side groups, [1,1';3',1''] terphenyl and phenyl[1,1';3',1''] terphenyl were substituted by Suzuki reactions. Thus, the side groups can be extensively applied for incorporating them in other core molecular structures UV and PL spectra of the synthesized compounds in the CHCl₃ solution state and the thin-film state are shown in Table 1 and Figure 1. In the CHCl₃ solution state, all of the synthesized materials exhibit UV_{max} value of 372–412 nm and PLmax values in the range of 441-450 nm. However, in the film state, the PL spectra of all these materials are red-shifted. Especially, TP-DTA-TP substituted with m-terphenyl was observed with an excimer peak. However, excimer peak was not observed in TPB-DTA-TPB substituted with bulky triphenylbenzene group. Accordingly, as the side group becomes bulkier, excimer is prevented by reducing intermolecular interaction and emission width is narrowed. In order to accurately interpret the EL efficiency of each material, the relative QE values of the side groups were measured [20]. The following QE results were

S. Kang et al.

	Soluti	on ^[a]	Film		
Compounds	UV _{max} (nm)	PL _{max} (nm)	UV _{max} (nm)	PL _{max} (nm)	
TP-DTA-TP	372, 391, 412	441	394, 414	459, 515	
TPB-DTA-TPB	392, 410	450	397, 413	460	

Table 1. Optical properties of synthesized materials

[a]: Chloroform solution $(1.0 \times 10^{-5} \text{ M})$

found for the solution state: m-terphenyl (0.10) < triphenylbenzene (0.17). Thus there are close correlations between the side group PL QE and the EL efficiency of the final compounds.

The HOMO and LUMO electron densities of TP-DTA-TP, TPB-DTA-TPB were determined with DFT/B3LYP/6-31G* calculations by carrying out optimization and time



Figure 1. (a) UV&PL spectra of TP-DTA-TP and TPB-DTA-TPB in solution state (Chloroform 10^{-5} M), (b) UV&PL spectra of TP-DTA-TP and TPB-DTA-TPB in film state.

[281]/71



Scheme 1. Chemical structures of the synthesized compounds.

dependent DFT (TDDFT) using Gaussian 03. The synthesized materials were shown to have HOMO and LUMO electrons located in anthracene in Figure 2.

We fabricated EL devices with the synthesized compounds in the following configuration: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials (35 nm)/Alq3 (20 nm)/LiF (1 nm)/Al (200 nm). EL performance of the devices is summarized in Table 2. Electrochemical cyclic voltammetry (CV) was performed to determine the highest occupied molecular orbital (HOMO) energy levels of the synthesized materials. The lowest unoccupied molecular orbital (LUMO) energy levels were obtained from the HOMO levels and the optical band gaps. The luminance efficiency (cd/A), power efficiency (lm/W) of the devices increase in the following order: TP-DTA-TP < TPB-DTA-TPB. Interestingly, this order is



Figure 2. HOMO and LUMO levels of (a) TP-DTA-TP, (b) TPB-DTA-TPB calculated at the DFT/B3LYP/6-31G* for optimization and Time Dependent DFT (TDDFT) using Gaussian 03.

Emitting Materials	Volt ^[a] (V)	C.E. ^[b] (cd/A)	P.E. ^[c] (lm/W)	C.I.E ^[d] (x, y)	EL _{max} (nm)	HO MO (eV)	LU MO (eV)	E _g ^[e] (eV)	T _d ^[f] (°C)
TP-DTA-TP	9.27	3.58	1.34	0.36, 0.53	521, 552	5.59	2.75	2.84	452
TPB-DTA-TPB	8.71	4.85	1.96	0.17, 0.23	475	5.60	2.78	2.82	468

Table 2. EL performances of multilayered devices with the synthesized compound at 10 mA/cm^2 and the optical, electrical and thermal properties of the synthesized materials

[a]: turn on voltage, [b]: current efficiency, [c]: power efficiency, [d]: Commission International de l'Eclairage, [e]: band gap, [f]: TGA at a heating rate of 10 $^{\circ}$ C /min

identical to the order of the PLQE values for the side groups. Moreover, it is interesting that the operating voltages of the devices decrease under the same current density conditions as the side group changes from m-terphenyl to triphenylbenzene (Figure 3(a)). In other words, the changes in the side groups of the compounds increase the power efficiency and



Figure 3. (a) I-V-L characteristics of TP-DTA-TP, TPB-DTA-TPB, (b) Normalized EL spectra of TP-DTA-TP, TPB-DTA-TPB.

luminescence efficiency properties. The normalized EL spectra of the fabricated EL devices are shown in Figure 3(b). As for the PL spectra, excimer peak was also disappeared from the EL spectra.

Conclusion

We have synthesized new anthracene derivatives with EL luminescence properties that were tuned in detail by varying the bulky side groups. As the luminescence efficiency of the side groups increases, the performance of the synthesized blue light emitters also improves substantially. TP-DTA-TP device showed C.I.E. value of (0.36, 0.53) and luminance efficiency of 3.58 cd/A at 10 mA/cm². TPB-DTA-TPB device exhibited C.I.E. value of (0.17, 0.23) and high luminance efficiency 4.85 cd/A at 10 mA/cm². TPB-DTA-TPB was found to show better luminance efficiency and C.I.E. value than TP-DTA-TP device because it had increased size of the side group.

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