

Synthesis and Characterization of Novel Blue Materials based on Anthracene Derivatives for High Efficient OLED

QingHua Zhao¹, Sung-Ouk Jung¹, Dong-Min Kang¹, Yun-Hi Kim², and Soon-Ki Kwon^{*1}

¹School of Nano and Advanced Materials Engineering, Gyeongsang National University, Jinju 660-701, South Korea

TEL:82-55-751-5296, *e-mail: skwon@gnu.ac.kr.

²Department of Chemistry, Gyeongsang National University, Jinju 660-701, South Korea

Keywords : blue light emitting

Abstract

Novel blue materials based on anthracene derivatives were synthesized by Grignard reaction, the Suzuki coupling reaction, etc. They showed excellent thermal stability and emitted bright blue light, which will be used for OLED and expected to obtain high efficiency and good color purity.

1. Introduction

OLEDs have attracted a great deal of attention because of their promising applications in full-color flat-panel displays,^[1-2] since the first application of the multilayer thin-film structures in organic light-emitting diodes (OLED) by Tang et al. During the past years, many new materials with RGB (red, green, blue) emission have been developed to meet the requirements of full-color displays. Compared with green-emitting, the electroluminescence (EL) characteristics of blue and red-emitting have to be improved particularly in terms of efficiency and color purity for full color application. It is much more difficult to produce blue emission due to its intrinsic of having a wide bandgap, irrespective of the type of materials. It is well known that electroluminescence (EL) efficiency can be significantly improved by using host-guest system^[3-4]. Up to date, many blue emitters based on fluorene or anthracene have been reported. For example, in our lab, some blue emitters based on anthracene derivatives also have been reported and achieve higher efficiency of 1.43 lmW⁻¹ (3.0 CdA⁻¹ at 6.6 V), such as BTSA⁵, BDSA⁵ and TBSA⁶. In this report, we synthesized blue materials based on anthracene derivatives, which would be used for doped or non-doped OLED and compared further. Good performance from these doped or non-doped devices was expected to obtain, not only anthracene derivatives have high photoluminescence (PL) and EL

efficiency, but also both of host and dopant based on anthracene derivatives can decrease solid self-aggregation (only host or dopant) to improve device performance, which often happen in device of host or dopant based on different types of materials.

2. Experimental

Materials. Anthracene, n-Butyllithium, fluorene and aluminium chloride (AlCl₃) were purchased from Aldrich. Tetrakis(triphenylphosphine)palladium was purchased from stem. All reagents purchased commercially were used without further purification. Tetrahydrofuran (THF) and diethylether were dried over sodium/benzophenone.

Measurements. A Genesis II FT-IR spectrometer was used to record IR spectra. ¹H-NMR and ¹³C-NMR spectra were recorded with the use of Avance 300 and DRX 500 MHz NMR Bruker spectrometers, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA instrument 2050 thermogravimetric analyzer. The sample was heated using a 10 °C/min heating rate from 50 °C to 700 °C. Differential scanning calorimeter (DSC) was conducted under nitrogen on a TA instrument 2100 differential scanning calorimeter. The sample was heated with the 10 °C/min from 30 °C to 300 °C. UV-vis absorption spectra and photoluminescence (PL) spectra were measured by Perkin Elmer LAMBDA-900 UV/VIS/NIR spectrophotometer and LS-50B luminescence spectrophotometer, respectively. Cyclic voltammograms of the polymer films were recorded on a epsilon E3 at a room temperature in a 0.1 M solution of tetrabutylammonium perchlorate (Bu₄NClO₄) in acetonitrile under nitrogen gas protection at a scan rate of 50 mV/s. A Pt wire was

used as the counter electrode and a Ag/AgNO₃ electrode as the reference electrode.

Synthesis.

Dimethylfluorene (1). Fluorene (11.7 g, 70 mmol), potassium t-butoxide (30 g, 210 mmol) and DMSO (300 mL) were added to 3-neck of 500 mL flask under nitrogen. After the temperature was cooled using ice bath, iodomethane (30 g, 210 mmol) was injected slowly. Then the reaction mixture was stirred for 12 h at room temperature and poured into water. After extracted with hexane and washed several times with water to remove DMSO, the organic mixture was dried by magnesium sulfate (MgSO₄). The purification was accomplished by column using hexane as eluent. Yield: 13 g (95 %). ¹H-NMR (300 MHz, ppm) : 7.83 (m, 2H); 7.53 (m, 2H); 7.45~7.4 (m, 4H); 1.58 (m, 6H).

(4-Bromophenyl)-(9,9-dimethyl-9H-fluoren-2-yl)-methanone (2). **1** (8 g, 40 mmol), aluminium chloride (7.13 g, 52 mmol) and carbon disulfate (CS₂) were added to 3-neck 250 ml flask under nitrogen. After the temperature was cooled using ice bath, 4-bromobenzoyl chloride (9.9 g, 45 mmol) dissolved in CS₂ was dropped slowly. Then the reaction mixture was stirred for 6 h at room temperature and terminated with an aqueous solution of 2N HCl. The reaction was extracted with methylene chloride (MC) and washed several times with water. The crude product was recrystallized in hexane to obtain pure product. Yield: 11 g (70 %). ¹H-NMR (300 MHz, ppm) : 7.91~7.82 (m, 4H); 7.80~7.65 (m, 4H); 7.39 (m, 3H).

(9,9-Dimethyl-9H-fluoren-2-yl)-phenyl-methanone (3). **1** (4 g, 20 mmol), aluminium chloride (3.5 g, 26 mmol) and carbon disulfate (CS₂) were added to 3-neck 250 ml flask under nitrogen. After the temperature was cooled using ice bath, benzoyl chloride (3.18 g, 23 mmol) dissolved in CS₂ was dropped slowly. Then the reaction mixture was stirred for 6 h at room temperature and terminated with an aqueous solution of 2N HCl. The reaction was extracted with methylene chloride (MC) and washed several times with water. The crude product was recrystallized in hexane to obtain pure product. Yield: 4.5 g (73 %). ¹H-NMR (300 MHz, ppm) : 7.98 (s, 1H); 7.9 (m, 1H); 7.86 (m, 1H); 7.8 (d, 2H); 7.53 (d, 1H); 7.45 (m, 3H); 7.35 (m, 2H).

2-[2-(4-Bromophenyl)-1-phenylvinyl]-9,9-dimethyl-9H-fluorene (4). **3** (0.97 g, 3.2 mmol) and 4-bromobenzylphosphonate (1.2 g, 3.9 mmol) in THF (50 mL) were added to 3-neck of 300 mL flask under nitrogen. After heated to 60 °C, potassium t-butoxide

(0.9 g, 8.1 mmol) dissolved in THF (20 mL) was dropped slowly. Then the reaction was refluxed for 4 h and terminated with aqueous solution of HCl (2 N). After extracted with hexane, the reaction was washed several times with sodium bicarbonate solution and water. The purification was accomplished using column. Yield : 1.05 g (75 %). ¹H-NMR (300 MHz, ppm) : 7.74 (d, 1H); 7.64 (d, 1H); 7.46 (m, 2H); 7.42~7.30 (m, 5H); 7.25~7.23 (m, 5H); 6.95 (m, 3H).

Anthracene 9, 10-dibromo acid (5). N-Butyllithium (30 mL, 75 mmol) was added to a solution of 9,10-dibromoanthracene (29.94 mmol) in anhydrous ether (100 mL) at -78 °C. The mixture was stirred at room temperature for 3 h. After the reaction mixture was cooled to -78 °C, triethylborate (144 mmol) was added to the reaction mixture. After stirring for 8 h, the reaction mixture was added to an aqueous solution of 2N HCl. The mixture was stirred for 1 h to produce a solid. The solid was filtered and washed several times with ether. The solid was recrystallized in ethyl acetate. Yield: 31 %. ¹H NMR (500 MHz, CDCl₃): 8.0 (d, 2H); 7.9 (d, 2H); 7.45 (m, 4H); 3.8 (4H).

[4-{10-[4-(9,9-Dimethyl-9H-fluorene-2-carbonyl)-phenyl]-anthracene-9-yl}-phenyl]-[9,9-dimethyl-9H-fluoren-2-yl]-methanone (6). **2** (5 g, 12.4 mmol) and **5** (1.05 g, 5.6 mmol) were mixed in a solution of THF (50 mL) and 2M K₂CO₃ (10 mL). After the mixture was degassed with nitrogen for 30 min, Pd(pph₃)₄ (0.26 g, 0.2 mmol) was added. Then the mixture was refluxed for 24 h and terminated with an aqueous solution of 2N HCl. After the mixture was extracted with methylene chloride and dried by MgSO₄, the pure product was separated using column. Yield: 2.2 g (70 %). ¹H-NMR (300 MHz, ppm) : 8.0 (d, 2H); 7.9 (s, 2H); 7.88 (d, 2H); 7.81 (d, 2H); 7.79~7.72 (m, 6H); 7.58 (d, 4H); 7.35~7.33 (m, 10H).

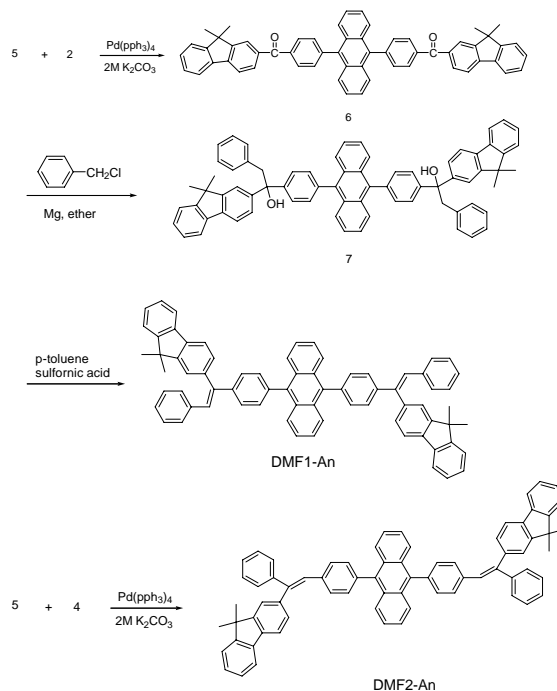
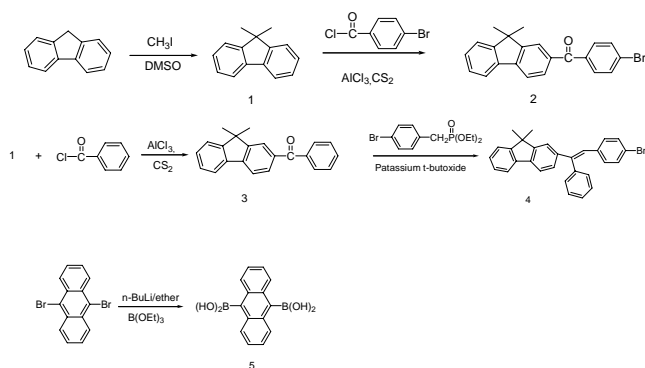
9,10-Bis-[4-[1-(9,9-dimethyl)-9H-fluoren-2-yl]-2-phenyl-vinyl]-phenyl-anthracene (DMF1-An). Benzyl chloride (1.64g, 13 mmol) and Mg (0.34 g, 14 mmol) were mixed in diethyl ether and refluxed for 1 h to get grignard reagent. After **6** (2g, 3 mmol) dissolved in diethyl ether was dropped slowly into the solution at room temperature, the reaction mixture was stirred for 2 h. Then the reaction was poured into ammonium chloride, extracted with ethyl acetate (EA). The crude product was dehydrated to give **7**. The dehydration was carried out by p-toluene sulfonic acid in benzene. The mixture was refluxed for 2 h. The water and benzene azeotrope was removed by a trap. The solution was neutralized by NaHCO₃. After the benzene was evaporated, the crude product was extracted by methylene dichloride. After the crude

product was purified by column, the product was recrystallized in ethanol. Yield: 1.8 g (70%). $^1\text{H-NMR}$ (300 MHz, ppm): 8.0~7.8 (m, 8H); 7.75 (m, 2H); 7.54~7.42 (m, 20H); 7.37~7.26 (m, 8H); 7.16 (d, 4H); 1.67 (s, 6H); 1.45 (s, 6H).

9,10-Bis-{4-[2-(9,9-dimethyl-9H-fluoren-2-yl)-2-phenylvinyl]-phenyl}-anthracene (DMF2-An). 4 (3.4 g, 7.5 mmol) and 5 (1.0 g, 3.8 mmol) were mixed in a solution of THF (70 mL) and 2M K_2CO_3 (10 mL). After the mixture was degassed with nitrogen for 30 min, $\text{Pd}(\text{pph}_3)_4$ (0.17 g, 0.1 mmol) was added. Then the mixture was refluxed for 24 h and terminated with an aqueous solution of HCl (2 N). After the mixture was extracted with MC and dried by MgSO_4 , the pure product was separated using column. Yield: 1.2 g (60%). $^1\text{H-NMR}$ (300 MHz, ppm): 7.9~7.7 (m, 8H); 7.7~7.6 (m, 6H); 7.6~7.25 (m, 20H); 7.26~7.21 (m, 6H); 1.6 (m, 6H); 1.52 (m, 6H).

3. Results and discussion

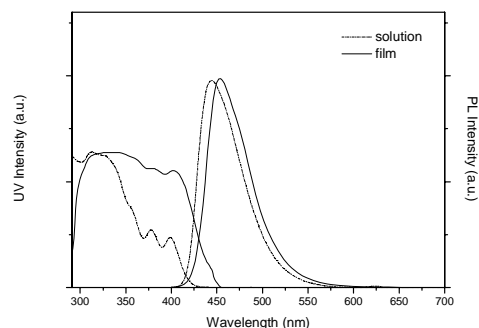
The DMF1-An and DMF2-An were prepared via a manifold chemical reaction such as Grignard reaction, Suzuki coupling reaction, etc, shown in scheme 1. Fluorene was treated with methyl iodide to give dimethylfluorene by alkylation reaction, and further reacted with 4-bromobenzoylchloride to get compound 2. The obtained compound 2 was treated with anthracene diboronic acid to obtain compound 6. DMF1-An was synthesized from compound 6 and benzyl magnesium bromide by a Grignard reaction, followed by reduction. Dimethylfluorene was treated with benzoylchloride to give compound 3, and compound 4 was synthesized from compound 3 by Wittig reaction. DMF2-An was obtained by reacting compound 4 with anthracene diboronic acid by Suzuki coupling reaction.



Scheme1. Synthetic routes for DMF1-An and DMF2-An.

The photophysical properties for these compounds were investigated from UV absorption and PL spectrum. Figure 1 showed UV-vis and PL spectra of DMF1-An and DMF2-An. Upon UV excitation at 380 nm, DMF1-An showed maximum PL peaks at 444 nm in solution and at 453 nm in solid. DMF2-An showed maximum PL peaks at 455 nm in solution and at 463 nm in solid, and red-shift for PL, compared with DMF1-An, was investigated.

a)



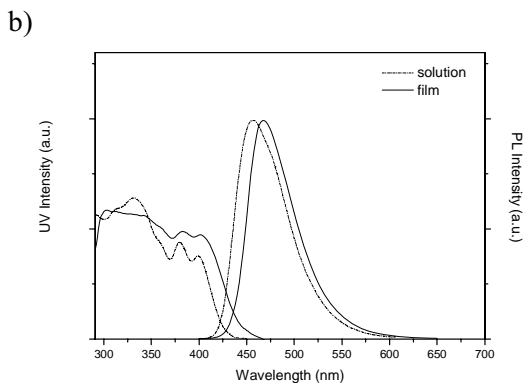


Figure 4.9. UV-vis and PL spectra for DMF1-An(a) and DMF2-An (b) in solution and in film.

The thermal properties of DMF1-An and DMF2-An were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in nitrogen, shown in Figure 2. Their decomposition temperatures, which correspond to a 5 % weight loss upon heating during TGA, are around 426 °C for DMF1-An and 425 °C for DMF2-An. They do not show any melting transitions (T_m), even when heated to 300 °C during DSC. In particular, their DSC exhibits a distinct T_g around 151 °C for DMF1-An and 154 °C for DMF2-An. This result indicates that the dimethylfluorene group might mitigate the intermolecular interactions among these molecules in the solid state. Consequently, DMF1-An and DMF2-An are able to form homogeneous and stable amorphous film by thermal evaporation, which is a basic requirement for materials to be used as OLEDs.

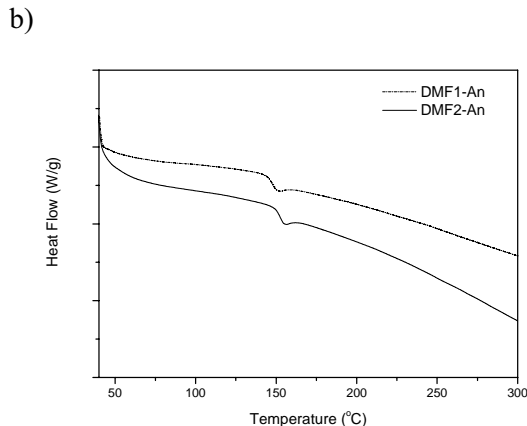
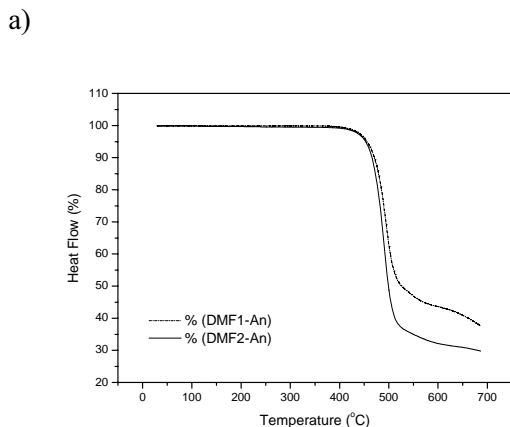


Figure 2. TGA and DSC curve of DMF1-An and DMF2-An.

4. Summary

A series of blue light emitting small molecule materials based on anthracene derivatives have been synthesized by Grignard reaction, Suzuki coupling reaction, etc. These materials showed bright blue emission and good thermal stability, which were used for OLEDs and expected to obtain high efficiency and blue light emitting from OLEDs.

5. Acknowledgements

This work was supported by the Information Technology Research Center (ITRC) under the Ministry of Information & Communications. Q. Zhao, S. Jung acknowledge the financial support of the Ministry of Education and Human Resources via the BK 21 Program.

6. References

1. J. Shi, C. W. Tang. *Appl. Phys. Lett.*, **70**, 1665 (1997).
2. L. S. Hung, C. H. Chen. *Mater. Sci. Eng. R*, **39**, 143 (2002).
3. C. W. Tang, S. A. Van Slyke, C. H. Chen. *J. Appl. Phys.*, **65**, 3610 (1989).
4. M. T. Lee, H. H. Chen, C. H. Liao, C. H. Tsai, *Appl. Phys. Lett.*, **85**, 3301(2004).
5. Y. H. Kim, H. C. Jeong, S. H. Kim, K. Y. Yang, S. K. Kwon. *Adv. Funct. Mater.*, **15**, 1799 (2005).
6. Y. H. Kim, D. C. Cheol, S. H. Kim, C. H. K, H. S. Yu, Y. S. Chae, S. K. Kwon. *Adv. Mater.*, **13**, 1690 (2001).