

Efficient Blue Light Emitting Diode by Using Anthracene Derivative with 3,5-Diphenylphenyl Wings at 9- and 10-Position

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The novel blue light emitting material, 9,10-bis(3',5'-diphenylphenyl)anthracene (BDA) was synthesized by Suzuki coupling reaction and characterized by the measurements of ¹H NMR, ¹³C NMR and FT-IR. The new anthracene derivative, which contains anthracene as a main core unit and 3',5'-diphenylphenyl group derivative as wings, has high fluorescence yield, good thermal stability, and high glass transition temperature at 188 °C. With the newly non-doped blue emitting material in the multilayer device structure, it was possible to achieve the current efficiency of 3.0 cd/A. The EL spectrum of the ITO/CuPc/ α -NPD/BDA/Alq₃/LiF/Al device showed a maximum wavelength (λ_{max}) at 440 nm. The emitting color of device showed the blue emission (x,y) = (0.18, 0.19) at 10 mA/cm² in CIE (Commission Internationale de l'Éclairage) chromaticity coordinates.

Key Words : Blue light emitting material, Anthracene

Introduction

Since the discovery of multilayered organic light emitting diodes (OLEDs) by Tang *et al.*¹ electroluminescent devices have been the subject of intensive investigation because of their applications in full-color displays.² For the full color display, three basic colors- red, green and blue- are needed. Particularly, in terms of efficiency and color purity for full color applications, the blue emitting devices have to be improved. Thus, recent various studies have been focused on improving the blue emitting material.³⁻¹²

Anthracene derivatives have interesting photo and electro-luminescent properties and good electrochemical properties.¹³ They have been extensively studied in applications such as light emitting diodes.¹⁴ However, 9,10-diphenylanthracene itself has an inherent problem of crystallization as a thin film in the device even it has near unity fluorescence quantum efficiency in the dilute solution and also has high fluorescence in the solid state. More recently, we reported deep blue OLEDs by using anthracene derivatives with bulky substituents in 9- and 10-positions of anthracene.¹⁵ The bulky substituents which are introduced in the 9- and 10-positions of anthracene are highly twisted to mitigate unfavorable steric interactions which limit the intermolecular interaction and lead to the pure blue emission. The introduced bulky substituents also lead the increased rigidity of molecules, which results in the high efficiency due to reduced vibronic mode and inhibited intermolecular interaction. In this article, we have newly designed novel blue light emitting material, 9,10-bis(3',5'-diphenylphenyl)anthracene (BDA), which contains anthracene as a main core unit and 3',5'-diphenylphenyl group derivative as wings. The introduction of 3',5'-diphenylphenyl "wing" which is rigid

and bulky, is expected to provide BDA with high efficient blue emission due to intramolecular energy transfer and inhibited intermolecular interaction.

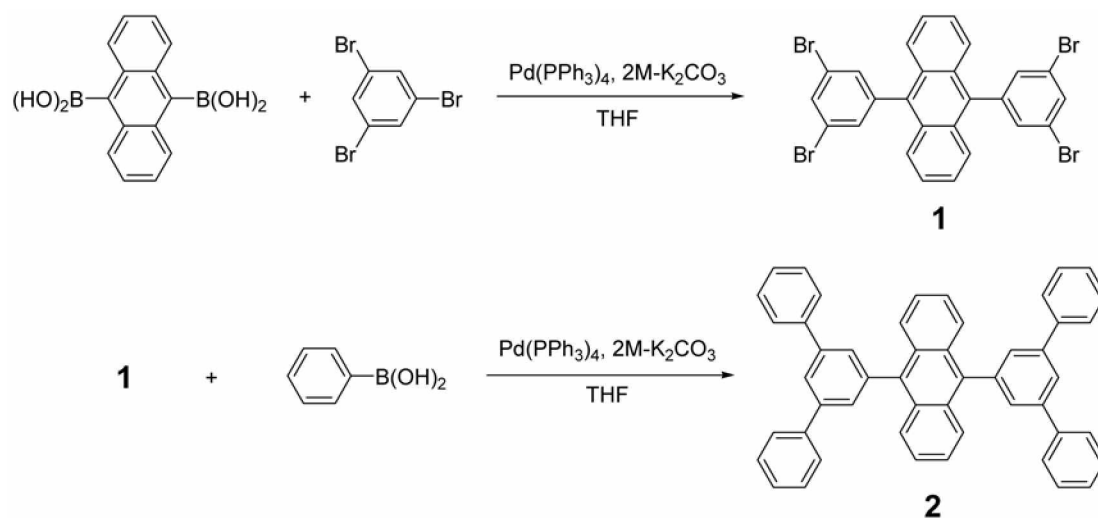
Experimental Section

General. All reagent and solvents were purchased from Aldrich Chemical Co. and Fluka. Only analytical grade quality chemicals were used. Spectroscopic grade CHCl₃ (Aldrich) was used for all absorption and emission experiments. All other compounds were used as received.

Synthesis of 9,10-Bis(3,5-dibromophenyl)anthracene (1). 1.2 g (4.7 mmol) of anthracene 9,10-diboronic acid and 7.4 g (20 mmol) of 1,3,5-tribromophenyl were mixed in THF solution. 50 mL of 2 M K₂CO₃ were added, and the mixture was stirred. The mixture was refluxed and 0.016 g of Pd(PPh₃)₄ were added and stirred for 72 h. After the crude solid product was filtered, it washed with water. The crude product was purified by column chromatography with hexane. Yield: 1.58 g (52%). ¹H-NMR (500 MHz, CDCl₃) δ [ppm] 7.9 (s, 2H), 7.9-7.7 (m, 4H), 7.6-7.4 (m, 6H). FT-IR (KBr, cm⁻¹): 3030 (aromatic C-H str), 1063 (aromatic C-Br).

Synthesis of 9,10-Bis(3',5'-diphenylphenyl)anthracene (BDA) (2). 0.5 g (0.77 mmol) of 9,10-bis(3',5'-dibromophenyl)anthracene and 0.47 g (3.87 mmol) of phenyl boronic acid were mixed in THF solution. 5 mL of 2 M K₂CO₃ were added, and the mixture was stirred. The mixture was refluxed, and 5.4 mg of Pd(PPh₃)₄ were added and stirred for 72 h. After the crude solid product was filtered, it washed with water. The crude product was purified by recrystallization with CH₂Cl₂ and Et₂O. Yield: 0.45 g (91%).

¹H-NMR (500 MHz, CDCl₃) δ [ppm] 8.0 (s, 2H), 7.9-7.8 (m, 4H), 7.7 (m, 12H), 7.5-7.4 (m, 8H), 7.3 (m, 8H). ¹³C-NMR



Scheme 1. Synthetic routes to BDA. The details are given in the experimental section.

(CDCl₃): aromatic (C) 142, 141, 140, 137, 130, 129, 128.3, 128.0, and 127.7, 127.4, 125.7, 125.5; FT-IR (KBr, cm⁻¹): 3030 (aromatic C-H str).

Results and Discussion

BDA was synthesized by Suzuki coupling reaction of phenyl boronic acid and 9,10-bis(3',5'-dibromophenyl)-anthracene which was also prepared by Suzuki coupling reaction of 9,10-anthracene diboronic acid and 1,3,5-tribromobenzene (Scheme 1). The structure of obtained compound was confirmed by ¹H-NMR and ¹³C-NMR. FT-IR, elemental analysis and mass spectra. Figure 1 showed the ¹H-NMR and ¹³C-NMR spectra of BDA. Theoretical

calculation using PM3 parameterization in the HyperChem 5.0 program (Hypercube), in order to fully optimize the molecular structure, was carried out for the characterization of 3-dimensional structures and the energy densities of HOMO and LUMO states of each material. Figure 2 shows the stereostructure of BDA derived from calculative analysis. Each substituents in 9- and 10-positions are highly twisted toward the anthracene backbone into an angle of 82.1. From this calculation, it is expected that the newly obtained material has non-coplanar structure which bears bulky substituents with the purpose of disrupting the intermolecular interaction and suppressing the problematic

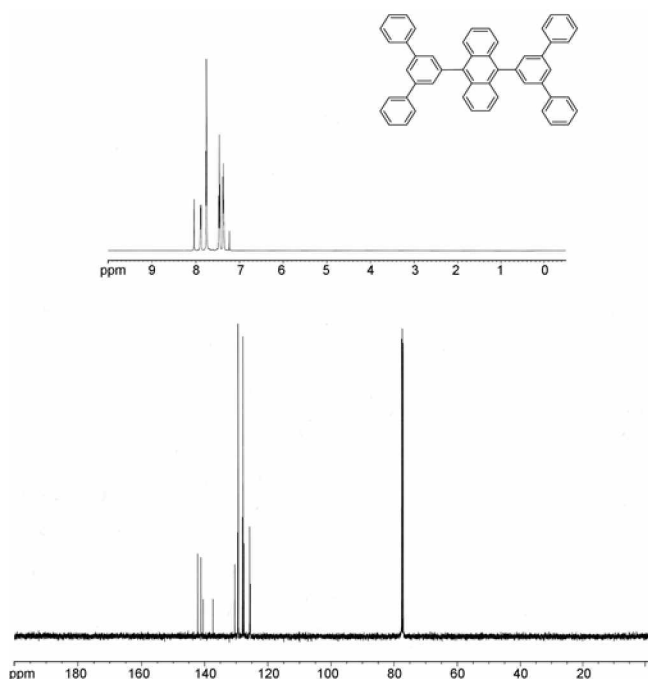


Figure 1. ¹H-NMR and ¹³C-NMR of BDA.

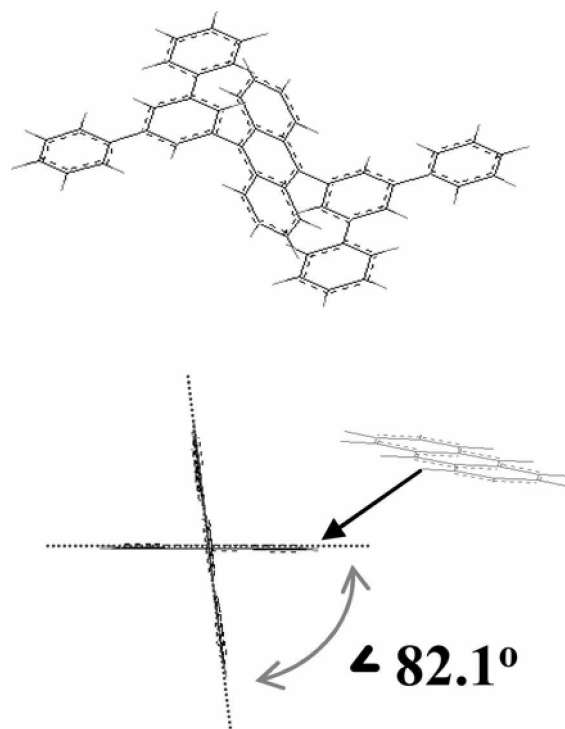


Figure 2. The stereostructures of BDA derived from calculative analysis.

recrystallization that would eventually reduce self-aggregation which, in turn, improve the morphological stability of the thin film of OLED device. The two 3',5'-diphenylphenyl group in the BDA "wings" make the compound soluble in common organic solvents such as chloroform, chlorobenzene, toluene and xylene even though they have very rigid structures. Differential scanning calorimetry (DSC) measurement shows that the glass transition temperature (T_g) of BDA occur at 188 °C. The 5% weight loss of BDA was observed at 380 °C. As a consequence, the obtained material is able to form homogeneous and stable amorphous film, a basic requirement for material to be used as material in OLEDs.

Figure 3 shows the optical spectra of BDA in solution and in thin film. The UV-visible absorption of BDA shows the characteristic vibrational patterns of side chain of 3',5'-diphenylphenyl group ($\lambda_{\max} = 260$) as well as the isolated anthracene group ($\lambda_{\max} = 346, 378, 399$ nm for BDA). When BDA is excited either at 260 and 378 nm, respectively, the same PL spectrum ($\lambda_{\max} = 415$ and 430 nm) is observed. According to the above result, it is carefully suggested that the intramolecular energy transfer occurred from 3',5'-diphenylphenyl group unit to anthracene. The nearly identical absorption spectra in solution and in film suggest that there is minimal intermolecular interaction in the ground state in thin film. The PL maximum of BDA represented at 415 nm and 430 nm for solution and 438 nm and 450 nm for film, respectively. Although there is difference in the relative peak intensity and a shift of 10-15 nm in peak positions, PL of solution and thin film exhibit pure blue emission and corresponding vibronic features. This difference may be caused by the different dielectric environment surrounding molecule. The obtained BDA exhibit very high PL quantum yields in solution. Φ_{sol} of material was determined by using standard procedure with blue quinine sulfate as reference. The determined Φ_{sol} (in CHCl_3) of BDA is 78%. The optical energy band gap of BDA is 2.96 eV, calculated from the threshold of the optical absorption ($\text{UV}_{\text{edg}} = 425$ nm).

Cyclic voltammetry (CV) is an easy and effective approach to measure redox reversibility and reproducibility. In addition, it can be utilized to evaluate simultaneously both HOMO

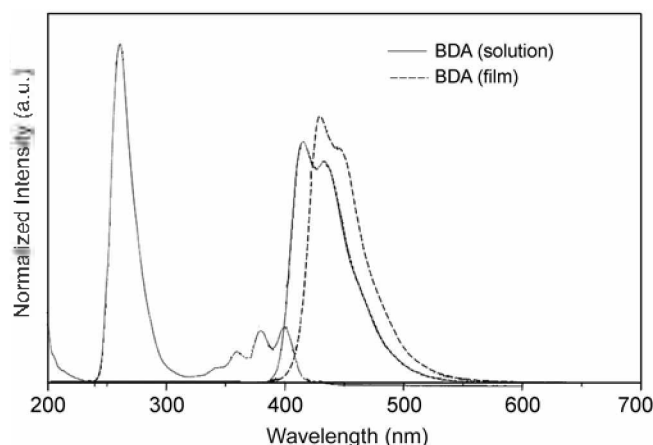


Figure 3. UV-vis and PL spectra of BDA.

and LUMO energy levels and band gap of a material. The oxidation peak potential of BDA was measured to be $E_{\text{ox}} = 1.32$ V. From the electrochemical data, the HOMO and LUMO are calculated at -6.12 eV and -2.87 eV, respectively.¹⁶

To study electroluminescent (EL) properties of highly efficient device by using obtained material as emitter, multi-layer device with the configuration glass/indium-tin-oxide anode/hole-injection layer (HIL)/hole-transporting layer (HTL)/emitting layer (EML)/electron transporting layer (ETL)/electron-injection layer (EIL)/Al cathode was fabricated. The copper phthalocyanine (CuPc) (20 nm) was used as HIL, 1,4-bis[(1-naphthylphenyl)-amino]biphenyl (α -NPD) (50 nm) as a HTL, DBA (40 nm) as an emitting layer, tris(8-hydroxyquinoline) aluminum (20 nm) (Alq_3) as an ETL, LiF (1nm) as an EIL and Al as an cathode. The current-luminance (I-L), voltage-current density (V-I) and current-efficiency (I-eff) characteristics of device based on BDA is shown in Figure 4. The turn-on voltage for 1 mA/cm^2 current injection was recorded at 4.5 V for device based on BDA as host. The light intensity was 300 cd/m^2 for 10 mA/cm^2 current injection and 1500 cd/m^2 for 100 mA/cm^2 current injection, respectively. The maximum electroluminescent efficiency of

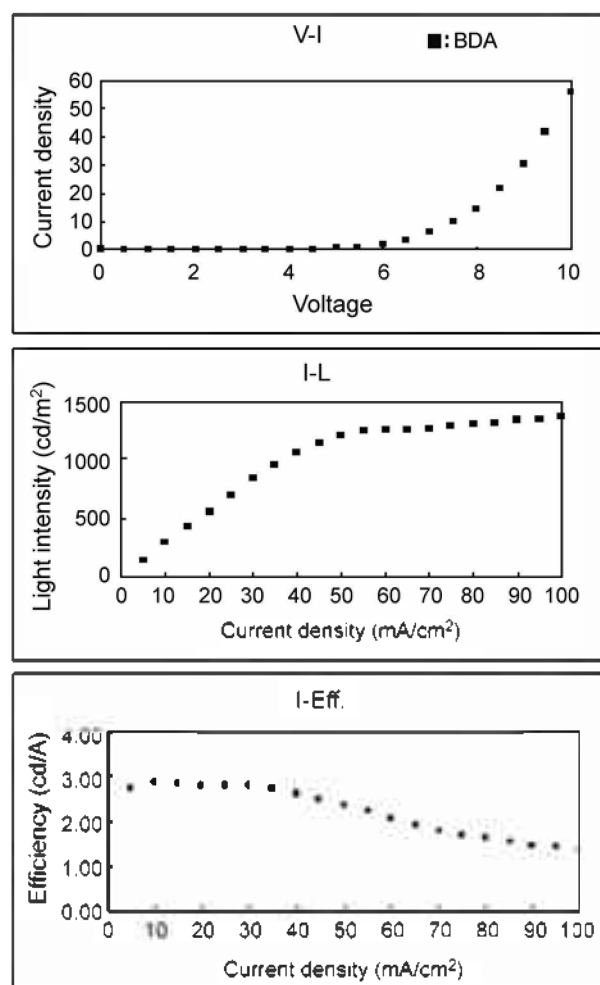


Figure 4. The current-luminance (I-L), voltage-current density (V-I) and current efficiency (I-Eff) characteristics of the device based on BDA.

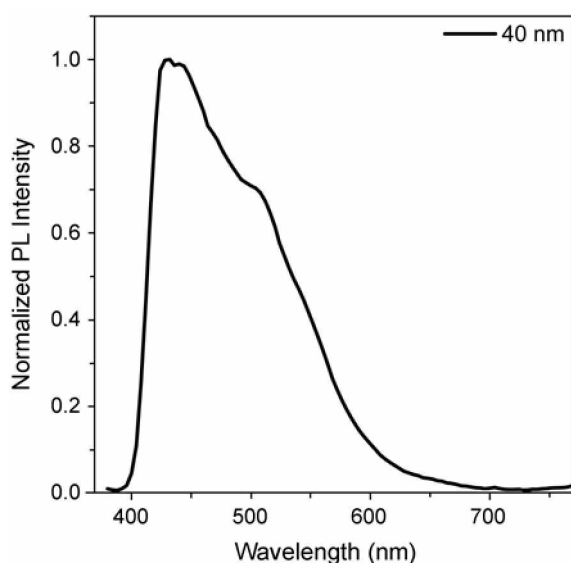


Figure 5. The electroluminescent spectrum of ITO/CuPc/ α -NPD/BDA/Alq₃/LiF/Al device.

device using BDA as emitting host material achieves 3.0 cd/A. The electroluminescence efficiency was constant as 3.0 cd/A up to 40 mA/cm² current injection. However, it was slightly decreased as increased current injection. The EL spectrum of the ITO/CuPc/ α -NPD/BDA/Alq₃/LiF/Al device showed in Figure 5 ($\lambda_{\text{max}} = 440$ nm.). The EL spectrum of device is shown in slightly broad and small long wave length emission. The emitting color of device showed the blue emission (x, y) = (0.18, 0.19) at 10 mA/cm² in CIE (Commission Internationale de l'Éclairage) chromaticity coordinates. In the future work, the efficiency and color purity of device will be improved by introduction of host-guest system.

Conclusion

We have designed and synthesized novel blue light emitting material which contains anthracene as a main core unit and 3',5'-diphenylphenyl group derivative as wings. The introduction of wings which rigid and bulky is expected to have high efficiency due to intramolecular energy transfer to anthracene unit and reduced vibronic mode as well as inhibited intermolecular interaction. The theoretical calculation supports that the obtained material has non-coplanar structure, which results in high PL efficiency, high quality of thin film and high thermal stability with high T_g. The non-doped devices using BDA as emitting material showed electroluminescence efficiency of 3.0 cd/A.

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