

Synthesis and Characterization of Novel Red-Light-Emitting Materials with Push-Pull Structure Based on Benzo[1,2,5]thiadiazole Containing Arylamine as an Electron Donor and Cyanide as an Electron Acceptor

Jin Uk Ju, Sung Ouk Jung, Qing Hua Zhao, Yun Hi Kim,^{†*} Jong Tae Je,[‡] and Soon Ki Kwon^{*}

School of Nano & Advanced Materials Science and Engineering and ERI, Gyeongsang National University, Jin Ju 660-701, Korea. *E-mail: skwon@gsnu.ac.kr

[†]Department of Chemistry and RINS, Gyeongsang National University, Jin Ju 660-701, Korea. *E-mail: ykimi@gnu.ac.kr

[‡]SFC CO., LTD. Ochang Techno Village 641-5, Cheongwon 363-883, Korea

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New efficient red emitter having short π -conjugation length and asymmetric bulky structure, 2-(7-diphenylamino-benzo[1,2,5]thiadiazole-4-ylmethylene)-malononitrile, was synthesized and characterized. Using this material as a dopant, we fabricated electroluminescence device with a structure of ITO/DNTPD/NPD/BTZA (5 wt% in Alq₃)/Alq₃/LiF/Al. The device exhibited a high brightness of 761 cd/m² at a driving voltage of 4.8 V, and current efficiency is 0.75 cd/A. The Commission International de l'Eclairage (CIE) coordinates of the EL device were found to be (0.62, 0.37) at 10 mA/cm².

Key Words : Benzo[1,2,5]thiadiazole, Push-pull, Inhibited intermolecular interaction, Amorphous

Introduction

Organic light-emitting diodes (OLEDs) have attracted a great deal of attention and numerous approaches to their fabrication have been proposed. OLEDs offer a number of advantages over conventional displays, such as faster response time, high efficiency, high color purity, low-voltage driving requirements, and simplicity.¹⁻⁵ Despite considerable progress that has been made over recent decades in this area, full-color OLEDs still require improvement in terms of efficiency, purity, durability, manufacturing process, and cost. These factors in turn depend on the evolution of high efficiency OLEDs materials, including RGB emitters.⁶⁻⁸ For realization of full-color, efficient emitting materials of all three primary colors (red, green, blue) are required.^{9,10} A number of green and blue emitting materials with reasonable color purity have been reported.¹¹ However, in comparison with green and blue emitting materials, red emitting materials remain deficient, owing to the following problems.^{12,13} First, the small energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the red-light emitters, results in non-radiative relaxation of the excited states.^{14,15} Second, the materials have several problems such as color-purity, stability, and efficiency, owing to the strong intermolecular dipole-dipole interactions or intermolecular π -stacking, as a result of their polar or extensive π -conjugated structures. This leads to a high tendency of aggregation and so-called concentration quenching.^{16,17} Consequently, most red OLEDs always use a dopant system. Third, most of the red light emitting materials are complicated and give the final product in low yield.¹⁸

In this paper, we report efficient red emitter having short π -conjugation length and asymmetric bulky structure, 2-(7-

diphenylamino-benzo[1,2,5]thiadiazole-4-ylmethylene)-malononitrile. The introduced triphenylamine is electron donating group to benzothiadiazole as well as hole transporting group, and the introduced malonitrile is electron withdrawing group as well as electron transporting group. Thus, the new red emitting material with push-pull structure is expected to have high efficiency by restraining intermolecular dipole-dipole interaction due to its bulky and asymmetric structure. Furthermore, it is also expected to have high efficiency due to a charge balance of the triphenylamine group, which serves as a hole transporting moiety, and the cyanide group, which functions as an electron transporting moiety.

Experimental Section

Synthesis

4-Bromo-benzo[1,2,5]thiadiazole (1) (BBTD). A mixture of benzo[1,2,5]thiadiazole (5.0 g, 36.8 mmol) in aq. HBr (48%, 15 mL) was heated to reflux with stirring, while Br₂ (2.8 mL, 110 mmol) was added slowly within 1 h. Towards the end of the addition, the mixture became a suspension. To facilitate stirring aq. HBr (48%, 10 mL) was added, and the mixture was heated to reflux for 2 h after completion of the Br₂ addition. The mixture was filtered while hot, cooled, filtered again, and washed well with H₂O. The compound was dried (Na₂SO₄) and recrystallized (MeOH) to afford **1** (6.3 g, 81%): ¹H NMR (300 MHz, CDCl₃) δ 8.00-8.03 (m, 1H), 7.81-7.84 (m, 1H), 7.43-7.50 (m, 1H).

4-Bromo-7-bromomethyl-benzo[1,2,5]thiadiazole (2) (BMTD). Compound **1** (5 g, 23.2 mmol) was dissolved in a mixture of 48% aqueous hydrobromic acid (100 mL) and glacial acetic acid (25 mL) and then trioxane (5 g, 56 mmol)

and trimethyl(tetradecyl)ammonium bromide (0.2 g) were added. The mixture was stirred and refluxed for 24 h. After cooling, the green solid was filtered and washed with water and ethanol. The compound was recrystallized (toluene) to afford **2** (5.4 g, 75%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.82 (d, 1H), 7.72 (s, 1H), 7.55 (d, 1H), 4.94 (s, 2H).

7-Bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde (3) (BBTC). Compound **2** (2.5 g, 10.3 mmol) was taken in a round bottom flask along with sodium periodate (NaIO_4) (0.42 g, 2 mmol). The above mixture was dissolved in 30 mL of *N,N*-dimethylformamide (DMF). The reaction mixture was heated at 150 °C. The progress of the reaction was monitored by thin layer chromatography by comparison with the starting material (10% ethyl acetate in hexane). The reaction was completed in 40 min. The reaction mixture was cooled and treated with 20 mL of water and then extracted with diethyl ether. The combined ether layers were dried over anhydrous magnesium sulfate (MgSO_4), then filtered off and concentrated. Evaporation of the solvent and purification by chromatography on silica gel (ethyl acetate/hexanes: 1:2). The compound was obtained **3** (2.2 g, 73.6%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 10.76 (s, 1H), 7.88 (d, 1H), 7.54 (d, 1H).

7-Diphenylamino-benzo[1,2,5]thiadiazole-4-carbaldehyde (4) (DBTC). Under nitrogen atmosphere of Compound **3** (2.0 g, 8.22 mmol), diphenylamine (1.99 g, 11.78 mmol), dppf (6.3 g, 12.33 mmol), NaOtBu (0.04 g, 0.41 mmol), and $\text{Pd}_2(\text{dba})_3$ (0.5 mol%) in toluene (30 mL) was stirred and heated at 120 for 8 h. After cooling to room temperature, saturated ammonium chloride solution was added to the reaction. The solution was extracted with ethyl acetate and dried over anhydrous magnesium sulfate (MgSO_4), then filtered off and concentrated. Evaporation of the solvent and purification by chromatography on silica gel (ethyl acetate/hexanes: 1:2). A greenish yellow solid was obtained **4** (2.1 g, 77.1%). $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 10.55 (s, 1H), 8.08 (d, 1H), 7.33-7.39 (m, 4H), 7.27 (t, 2H), 7.13-7.17 (m, 4H), 7.08 (d, 1H).

2-(7-Diphenylamino-benzo[1,2,5]thiadiazole-4-ylmethylene)-malononitrile (5) (BTZA). Compound **4** (2 g, 4.23 mmol), malononitrile (0.81 g, 8.45 mmol), and basic aluminium oxide (2 g) are stirred in toluene (20 mL) for 8 h at 70 °C. After cooling to room temperature, the reaction solution was filtered. The filtrate was subjected to flash column chromatography (silica gel, dichloromethane/hexanes: 1:2). A red solid was obtained **5** (1.62 g, 70.7%) $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.64-8.71 (m, 3H), 7.96-8.02 (m, 2H), 7.82 (t, 1H), 7.63-7.68 (m, 2H), 7.44-7.52 (m, 3H), 7.15 (d, 1H); EI-MS *m/z* (relative intensity) 379 (M^+ , 100.0), 380 (27.97), 381 (7.8), 382 (1.47). Analysis Calcd. for $\text{C}_{22}\text{H}_{13}\text{N}_5\text{S}$: C, 69.64; H, 3.45; N, 18.46; S, 8.45. Found: C, 69.72; H, 3.62; S, 8.87. FT-IR (KBr, cm^{-1}): 3010 (aromatic C-H), 2253 (C \equiv N), 1587 (C=N), 1542, 1495 (C=C), 1235 (C-N).

Instruments for characterization. The $^1\text{H NMR}$ spectra were recorded with a Bruker AM-200 spectrometer. The FT-IR spectra were measured on a Bomem Michelson series FT-IR spectrometer. The mass spectrometry (MS) were mea-

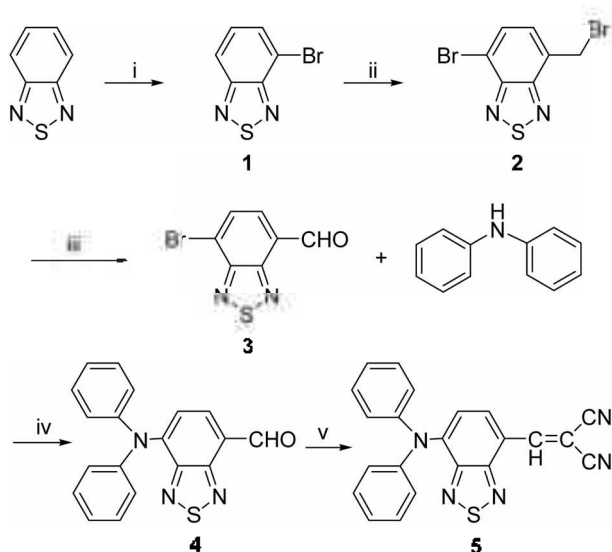
sured on a JMS-700. The melting points were determined with an Electrothermal model 1307 digital analyzer. The thermal analysis were performed on a TA TGA 2100 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 20 °C/min. Differential scanning calorimetry (DSC) was conducted under nitrogen on a TA Instrument 2100 differential scanning calorimeter. The sample was heated at 20 °C/min from 30 to 220 °C. UV-vis absorption spectra and photoluminescence spectra were measured with a Perkin-Elmer Lambda-900 UV-vis/IR spectrophotometer and an LS-50B luminescence spectrophotometer, respectively. The photoluminescence spectra were reacted on a PerkinElmer LS-50 fluorometer with a lock-in amplifier system with a chopping frequency of 150 Hz. Cyclic voltammetry was performed on an EG&G Parc 273-Å potentiostat/galvanostat system with a three-electrode cell in a solution of Bu_4NClO_4 (0.1 M) in acetonitrile at a scanning rate of 100 mV/S.

Organic light-emitting diode (OLED) fabrication. Pre-patterned indium tin oxide (ITO) substrates were cleaned by sonication in a detergent solution for 2 min and then washed with a large amount of doubly distilled water. Further sonication in ethanol for 2 min was done before blowing dry with a stream of nitrogen. The ITO substrates were then treated with O_2 plasma for one minute before being loaded into the vacuum chamber. The organic layers were deposited thermally at a rate of 0.1-0.3 nm s^{-1} under a pressure of about 10^{-6} torr. OLEDs devices were constructed with 60 nm of DNTPD as the hole injection layer, 20 nm of NPD as the hole transporting layer, 20 nm of BTZA (5 wt% in Alq_3) as the emission layer, 40 nm of Alq_3 as the electron transporting emission layer, 0.5 nm of LiF as the electron injection layer and 50 nm of Al as the cathode. The EL was measured under ambient conditions.

Results and Discussion

The overall synthetic routes are outlined in Scheme 1. As shown in Scheme 1, compounds 1-5 were prepared with highly overall yields. Bromination of **1** by bromine afforded 4-bromo-benzo[1,2,5]thiadiazole (**1**) (**BBTD**) with 81% yield. 4-Bromo-7-bromomethyl-benzo[1,2,5]thiadiazole (**2**) (**BMTD**) was obtained by allylic bromination. 7-Bromo-benzo[1,2,5]thiadiazole-4-carbaldehyde (**3**) (**BBTC**) was obtained by a formylation reaction through allylic bromination. The following arylamination of the aldehyde-carrying 7-diphenylamino-benzo[1,2,5]thiadiazole-4-carbaldehyde (**4**) (**DBTC**) was readily performed in the presence of 1,1'-bis(diphenylphosphino)ferrocene, NaOtBu , $\text{Pd}_2(\text{dba})_3$, and diphenylamine. Toluene was found to be the most suitable as reaction solvent with 77.1% yield. Finally, malononitrile was condensed in Knoevenagel conditions (basic Al_2O_3 in dry toluene) with aldehyde with **4** to form the dicyanovinyl electron-withdrawing group of the red emitting 2-(7-diphenylamino-benzo[1,2,5]thiadiazole-4-ylmethylene)-malononitrile (**5**) (**BTZA**) compound. Our strategy was successfully carried out with high yield.

The resulting compounds were examined by spectroscopy



Scheme 1. Synthetic procedure for the emitter. Reagent i, HBr, Br₂; ii, trioxane, trimethyl(tetradecyl)ammonium bromide, HBr, AcOH; iii, NaIO₄, DMF; iv, dppf, NaOtBu, Pd₂(dba)₃, diphenylamine, toluene; v, malononitrile, basic Al₂O₃, toluene.

analyses. The structure of BTZA was identified by ¹H NMR, FT-IR, mass spectrometry (MS), and elemental analysis. The thermal properties of BTZA were examined *via* a thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Despite being a small molecule, BTZA showed a glass transition temperature of 130 °C, suggesting that the material could form homogeneous and amorphous film through thermal evaporation. The 5% weight loss of BTZA was observed at 267 °C.

The optical properties of BTZA were examined using UV-vis and photoluminescence (PL) spectra. Figure 1 shows the normalized UV-vis absorption and PL spectra of BTZA. The absorption maximum of BTZA was observed at 532 nm for solution and 561 nm for film, respectively. A red shift in the absorption maxima was observed from solution to film, which was similar with solvato chromic effect, indicating that this molecule exhibits intramolecular charge transfer character in the ground state.¹⁹ The optical band gap of

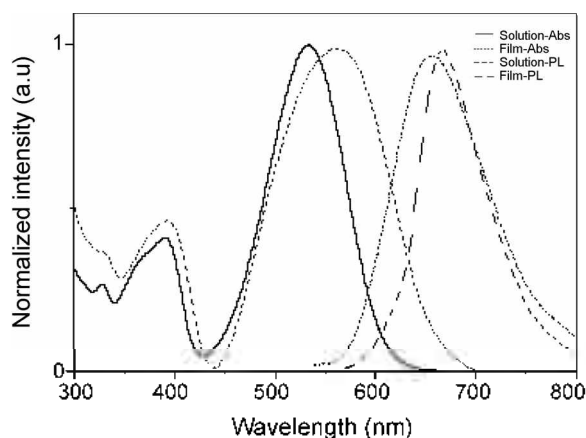


Figure 1. Normalized UV-vis spectra absorption and photoluminescence spectra of BTZA.

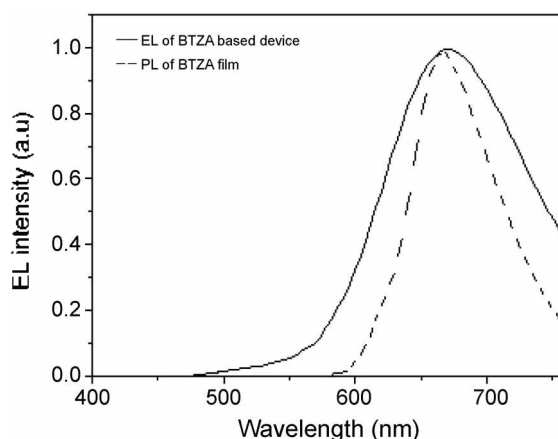


Figure 2. PL and EL spectra of the BTZA.

BTZA was 2.07 eV, calculated from the threshold of the absorption edge at 599 nm. The PL maximum of BTZA was found at 655 nm for solution and 665 nm for film, respectively. Therefore, the new material emitted red emission despite having short conjugation. Moreover, it did not show shoulder emission at long wavelength due to the charge transfer complex and excimer formation. Electrochemical properties of BTZA were examined using cyclic voltammetry (CV). CV measurement of BTZA in 0.1 M solution of tetraammonium perchlorate (Bu₄NClO₄)/acetonitrile solution was carried out. A platinum plate was used as the working electrode, a platinum wire as the counter electrode, and Ag/Ag⁻ as the reference electrode.³⁰ The reduction onset of BTZA was -0.7 eV. Using this value, the LUMO of BTZA was calculated as -3.54 eV by ferrocene correction. From the LUMO and optical band gap, the HOMO level of BTZA was determined to be -5.61 eV. The EL properties of BTZA were investigated using a device fabricated with the following configuration: ITO/DNTPD/NPD/BTZA (5 wt% in Alq₃)/Alq₃/LiF/Al. ITO was employed as the anode, DNTPD for hole injection, NPD for hole transporting, BTZA (5 wt% in Alq₃) as the red emitting material, Alq₃ for

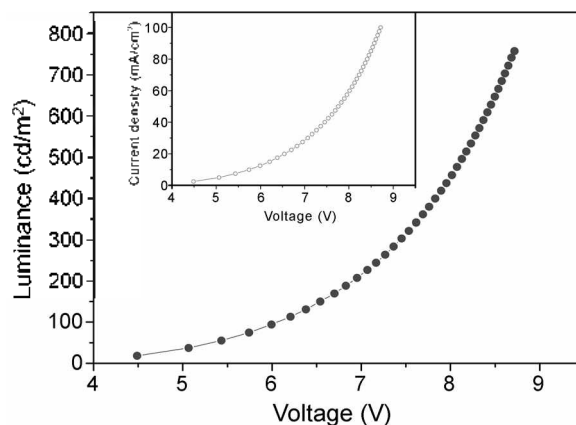


Figure 3. Luminance-voltage characteristics of ITO/DNTPD/NPD/BTZA (5 wt% in Alq₃)/Alq₃/LiF/Al. (Inset: Current-density characteristics).

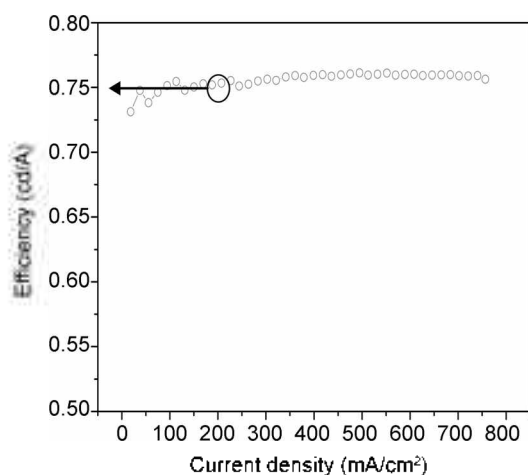


Figure 4. Efficiency versus current density of BTZA.

electron transporting, LiF for electron injection, and Al as the cathode.²¹ The EL spectrum of the device is shown in Figure 2. The EL maximum was at 671 nm. The Commission International de l'Eclairage (CIE) coordinates of the EL device were found to be (0.62, 0.37) at 10 mA/cm². The luminescence-voltage and current-voltage characteristics of the BTZA device are shown in Figure 3. The maximum brightness of BTZA was 761 cd/m² with a turn-on voltage of 4.8 V. Figure 4 shows the efficiency versus current density characteristics of the BTZA device. Here, we can observe stable efficiency (0.75 cd/A) even with increased current density. Device optimization is currently being carried out in order to increase the maximum brightness and efficiency.

In summary, we designed and synthesized 2-(7-diphenylamino-benzo[1,2,5]thiadiazole-4-ylmethylene)-malononitrile (**5**) (BTZA) as a red emitting material, where arylamine serves as an electron donor and cyanide plays the role of an electron acceptor (*i.e.*, a push-pull system). The new red emitting material was simply and successfully synthesized with high yield. BTZA emitted red light with a peak at 671 nm and CIE coordinates of (0.62, 0.37) at 10 mA/cm². The maximum brightness of BTZA was 761 cd/m² with a stable efficiency of 0.75 cd/A.

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