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Efficient deep blue fluorescent emitter showing high external quantum efficiency

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ABSTRACT

A benzoanthracene-cored deep blue-emitting compound, N^6,N^9-bis(4-cyano-phenyl)-N^3,N^9-diphenyl-spiro[benzo[*de*]anthracene-7,9′-fluorene]-3,9-diamine was synthesized and which has an exchange energy of ~0.2 eV between the singlet and triplet state. OLED devices doped with this new deep blue emitter showed comparable device performances and delayed fluorescence *via* the reoccupation of the singlet excitons from the triplet excitons with long lifetimes. In particular, the 10%-doped device exhibited the maximum external quantum efficiency of 14.8% and current efficiency of 15.1 cd/A with Commission International de L'Edairge coordinates of (0.14, 0.11).

1. Introduction

Over the past few decades, a lot of researchers have made breakthrough and significant progress on organic light-emitting diodes (OLEDs) which have been anticipated for the general lighting and/or the next-generation displays with the vivid colors, wide viewing angles, and application in flexible emitting devices [1–9]. However, relatively low external quantum efficiency (EQE) of OLEDs has remained an obstacle to compete with the inorganic LEDs, due to the light loss mechanism such as the substrate mode, waveguide mode, and surface plasmon mode [10–13]. The EQE is generally represented as:

$$EQE = \eta_{\mathrm{int}}\eta_{out} = \gamma\eta_e q_{eff}\eta_{out} \tag{1}$$

where γ represents the charge carrier balance at the emission layer, η_e is the fraction of excitons that contribute to radiative decay process, q_{eff} is the photoluminescence quantum efficiency determining the fraction of excited states decaying radiatively, and η_{out} is out-coupling efficiency representing the fraction of total light to escape from the light-emitting medium into the air. There have been numerous studies to improve η_{out} (typically 20–30%) in OLEDs, such as the micro lens array, two-dimensional periodic nanostructures, nano-scattering medium and the low-index grid approach [14,15]. Nevertheless, there is still a fundamental restriction to increase η_{out}, so that the importance of enhancing the internal quantum efficiency (η_{int}) is mostly highlighted.

For fluorescent OLEDs, η_e is assumed to be 25% based on spin statistics. This can increase up to 100% by using phosphorescent emitters containing the transition metals like iridium or platinum which causes strong spin–orbit coupling [16]. However, the operational lifetimes of the devices fabricated with such materials are rather shorter than those of the typical fluorescent devices, because a longer exciton lifetime of triplet species raises the possibility of the thermal and/or chemical degradation [17]. In addition, the host materials for the blue phosphorescent emitters usually lead to bond dissociation and make OLED devices less stable due to the high singlet energy level.

In this regard, many research groups have studied alternative ways to enhance η_{int}, especially by using fluorescent materials. As a result, the delayed fluorescence (DF) such as thermally activated delayed fluorescence (TADF) [18–21] and triplet–triplet annihilation (TTA) [22–25] has attracted an attention, which realizes η_{int} of 100% and 62.5%, respectively, compared to η_{int} of 25% in classical fluorescent emitter, because triplet excitons can be converted into

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singlet ones by reverse intersystem crossing (RISC). DF can provide highly efficient OLEDs, with the possibility to obtain the molecules with versatile design and relatively simple synthetic pathway [26–29], compared to the phosphorescent emitters [30–33]. In addition, fluorescent emitters show a fairly long operational lifetime, which is an advantage over the phosphorescent emitters. TADF is more competitive define TTA in terms of η_{int}, but the standard method for the TADF materials has not been well established despite the reports on the various types of materials [18–21]. Moreover, the TADF materials normally possess highly polar characteristics, which cause a bathochromic shift only with a slight variation of the dopant. Hence, the development of deep blue emitters with both TADF characteristics and good color stability turns out to be difficult. In contrast, TTA can be utilized to realize a highly efficient deep blue fluorescent OLED by employing pre-existing commercialized materials, so that DF through TTA can serve two ends in terms of the efficiency and color stability.

In this study, we developed new emitter for highly efficient deep-blue fluorescent OLED with EQE above 10%.

2. Experimental

2.1. Synthesis of new blue emitter

2.1.1. Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer and chemical shifts were referenced to chloroform (7.26 ppm). The absorption spectra were obtained by UV–vis spectrophotometer (JASCO V-570). The DSC measurements were performed on a Mettler DSC 823e under nitrogen at a heating rate of 10 °C/min (TA instruments) and thermogravimetric analysis (TGA) using TGA 50 (Shimadzu). Low and high resolution mass spectra were recorded using a LC-mass (Shimadzu LCMS-2020). Energy levels were measured with a low energy photoelectron spectrometer (Riken-Keiki AC-2). High resolution mass spectra were recorded using an JMS-700 in EI mode.

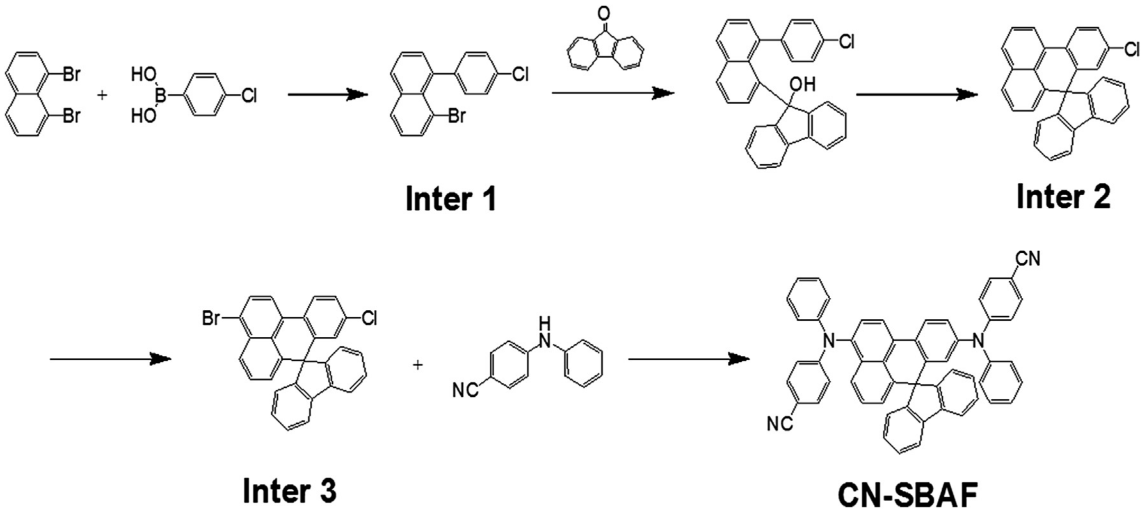
2.1.2. Synthetic details

The detailed synthetic method and analysis of 10-(naphthalene-2-yl)-3-(phenanthrene-9-yl)spiro[benzo[*ij*]tetraphene-7,9′-fluorene] (SBTF) were described in our previous report [34]. N^6,N^9-bis(4-cyanophenyl)-N^3,N^9-diphenylspiro[benzo[*de*]anthracene-7,9′-fluorene]-3,9-diamine (CN-SBAF) were newly synthesized and purified by standard process as shown in Scheme 1.

The detailed synthetic methods and analyses of CN-SBAF are available in supporting information.

*2.1.2.1. Synthesis of 1-bromo-8-(4-chlorophenyl)naphthalene **(Inter 1)**.* 4-Chlorophenylboronic acid (6.6 g, 40 mmol), 1,8-dibromonaphthalene (15 g, 50 mmol), tetrakis(triphenylphosphine) palladium(0) and THF (300 mL) were stirred in a two-necked flask for 30 min. Into the above solution, was added potassium carbonate (29 g, 210 mmol) dropwise over a period of 20 min. The resulting solution was refluxed overnight at 80 °C. The reaction mixture was extracted with dichloromethane and water. After the organic layer was evaporated with a rotary evaporator, the evaporated and resulting powdery product was purified by column chromatography using *n*-hexane to give a white crystalline solid. Yield 80% ^{1}H NMR (500 MHz, DMSO) 8.090–8.052 (t, 2H), 7.843–7.826 (d, J = 8.5 Hz, 1H), 7.624–7.594 (t, 1H), 7.448–7.388 (m, 5H), 7.299–7.280 (m, 2H) ppm. EI-MS [M+H]$^+$: 318.

*2.1.2.2. Synthesis of 9-chlorospiro[benzo[de]anthracene-7,9′-fluorene] **(Inter 2)**.* Into a 250 mL, two-necked flask, was placed a Inter 1 (10 g, 30 mmol) in THF (110 mL). The reaction flask was cooled to −78 °C and *n*-BuLi (2.5 M in hexane, 12.6 mL) was added dropwise slowly. The whole solution was stirred at this temperature for 1 h, followed by addition of a solution of 9-fluorenone (5.7 g, 31 mmol) in THF (23 mL) under argon atmosphere. The resulting mixture was gradually warmed to ambient temperature and quenched by saturated, aqueous $NaHCO_3$ (40 mL). The mixture was extracted with dichloromethane. The combined organic layers were dried magnesium sulfate, filtered, and evaporated under reduced pressure. The yellow powdery product was obtained. The crude residue was placed in other two-necked flask, and dissolved in acetic acid (200 mL). Catalytic amount of aqueous HCl (5 mol%, 12 N) was then added and the whole solution was refluxed for 12 h. After having been cooled to ambient temperature, the purification by silica gel chromatography using dichloromethane/*n*-hexane and gave a white powder. Yield 74%. T_g 113 °C. T_m 200 °C. ^{1}H NMR (500 MHz, DMSO) ^{1}H NMR (500 MHz, DMSO) 8.479–8.464 (d, J = 7.5 Hz, 1H), 8.442–8.424 (d, J = 9 Hz, 1H), 8.051–7.981 (m, 3H), 7.824–7.808 (d, J = 8 Hz, 1H), 7.735–7.704 (m, 1H), 7.451–7.389 (m, 3H), 7.298–7.268 (t, 1H), 7.214–7.184 (t, 2H), 6.912–6.897 (m, 2H) 6.481–6.466 (d, J = 7.5H, 1H) 6.269–6.264 (s, 1H) ppm. ^{13}C NMR



Scheme 1. Synthetic method for deep blue delayed fluorescent dopant, CN-SBAF.