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A New Orange-Light-Emitting Materials Based on (N-naphthyl)-1,8-naphthalimide for OLED Applications

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A new orange emitters consisting of 2-naphthalene-1-yl-benzo[de]isoquinoline-1, 3-dione (NBID) as core, and bulky diphenylamine or naphthylphenylamine substituted as a side units were synthesized and characterized. These compounds have a non-planar molecule conformation, donor-acceptor structure, and high thermal stability. Using these materials as dopant, we fabricated electroluminescence device with a structure of ITO/DNTPD/NPD/NBID-1, 2 (3 wt% in Alq₃)/Alq₃/ LiF/Al. The luminance-efficiency of NBID derivatives (1 and 2) were showed 6.6 cd/A and 5.9 cd/A, respectively. The orange emissions were observed with Commission International de l'Eclairage (CIE) coordinates of (0.46, 0.52) for NBID-1 and (0.48, 0.52) for NBID-2, respectively.

Keywords: amorphous; donor-acceptor structure; non-planar conformation; OLED; orange-emitter

INTRODUCTION

Since Tang's [1] and Burroughes's [2] pioneering work, organic light-emitting diodes (OLEDs) based on small molecules and polymers have attracted interest because of their potential application to full color flat panel displays [3–5]. For realization of full-color, organic materials

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emitting the three primary colors of red, green, and blue with high efficiency, good color purity are required [6–8]. Recently, much attention has been paid to OLEDs based on red and orange emitting materials [9]. Although there has been great progress on the development of new red fluorescent and phosphorescent materials [10], it remains to be the weakest part in realizing the full potential of full color OLED due to the low efficiency, poor color purity [11]. Therefore, many efforts have been made to improve the properties of red and orange materials [12].

In this article, we designed efficient orange emitter having short π -conjugation length. The triphenylamine or N,N-diphenylanphthalene-2-amine are electron donating group as well as hole transporting group, and isoquinoline is electron withdrawing group as well as electron transporting group. Therefore, the new orange emitting materials with donor-acceptor structure are expected to have high efficiency by controlling intermolecular dipole-dipole interaction due to its bulky and asymmetric structure.

EXPERIMENTAL

Synthesis

(N-naphthyl)-4-bromo-1,8-naphthalimide (NBID) [13]. To a solution of 4-bromo-1,8-naphthalic anhydride (5.0 g, 18.1 mmol) in m-cresol (70 mL) were added 1-naphthylamine (6.46 g, 45.1 mmol) and isoquino-line (4.66 g, 36.1 mmol). The mixture was stirred for overnight at 220°C. After completion of the reaction, resulting mixture was cooled, poured into methanol, and filtered. And then, the product was dissolved in chloroform and purified by column chromatography on silica gel using hexane/dichloromethane (3:1) as a eluent. Finally, the product was recrystallized from hexane. Yield: 5.2 g, 71%.

(N-naphthyl)-4-diphenylamino-1,8-naphthalimide (NBID-1) [14], To a 100 mL three-necked flask under nitrogen were added (a) diphenylamine $(0.70 \,\mathrm{g},$ $(1.00 \,\mathrm{g},$ 2.5 mmol), 3.0 mmol), $Pd(OAc)_2$ (0.07 g, 0.10 mmol), tri-tert-butyl phosphine (0.01 g, 0.04 mmol), and sodium tert-butoxide (0.36 g, 3.70 mmol). Toluene (10 mL) was then added to the flask *via* a syringe and the mixture was stirred for 24 h at 120°C. After completion of the reaction, resulting mixture was cooled and poured into water. The product was extracted with ethyl acetate. The organic layer was separated from the aqueous layer, washed with water, and brine sodium hydroxide. Furthermore, the product was dried over anhydrous MgSO₄. After removal solvent, the crude product was purified by column chromatography on silica gel using hexane/dichloromethane (5:1) as a eluent. Yield : 0.9 g, 73%, ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.59~8.65 (m, 2 H), 8.30~8.33 (m, 1 H), 7.94~8.04 (m, 2 H), 7.45~7.72 (m, 7 H), 7.28~7.36 (m, 4 H), 7.11~7.16 (m, 6 H); ¹³C NMR (300 MHz, CDCl₃), δ (ppm): 118.67, 122.02, 123.37, 123.87, 123.97, 125.55, 125.65, 126.29, 126.43, 126.76, 127.10, 128.19, 128.69, 129.41, 129.69, 130.22, 131.00, 131.73, 131.88, 132.48, 132.73, 134.57, 148.42, 151.41, 163.93, 164.51; Analalysis Calcd. for C₃₄H₂₂N₂O₂: C, 83.25; H, 4.52; N, 5.71; O, 6.52. Found: C, 83.31; H, 4.61; O, 6.46.

(N-naphthyl)-4-naphthalene-2-yl-phenyl)amino-1,8-naphthalimide (NBID-2) was synthesized by the same method with NBID-1. To a 100 mL three-necked flask under nitrogen were added (a) (1.00 g, 2.5 mmol), N-phenylnaphthalene-2-amine (0.70 g, 3.0 mmol), Pd(OAc)₂ (0.07 g, 0.10 mmol), tri-tert-butyl phosphine (0.01 g, 0.04 mmol), and sodium tert-butoxide (0.36 g, 3.70 mmol). Toluene (10 mL) was then added to the flask *via* a syringe and the mixture was stirred for 24 h at 120°C. After completion of the reaction, resulting mixture was cooled and poured into water. The product was extracted with ethyl acetate. The organic layer was separated from the aqueous layer, washed with water, and brine sodium hydroxide. Furthermore, the product was dried over anhydrous MgSO₄. After removal solvent, the crude product was purified by column chromatography on silica gel using hexane/dichloromethane (5:1) as a eluent. Yield: 1.0 g, 74%. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.64~8.65 (t, 1 H), 8.61~8.63 (t, 1H), 8.34~8.38 (m, 1H), 7.98~8.05 (m, 2H), 7.82~7.85 (t, 2H), 7.59~7.72 (m, 3H), 7.44~7.57 (m, 8H), 7.34~7.37 (m, 3H), 7.17~7.20 (t, 3 H); $^{13}\mathrm{C}$ NMR (300 MHz, CDCl_3), δ (ppm): 118.89, 120.61, 122.05, 123.42, 123.69, 124.11, 124.18, 125.26, 125.67, 125.76, 126.32, 126.59, 126.78, 127.12, 127.16, 127.74, 128.23, 128.71, 129.43,129.65, 129.78, 130.24, 130.46, 131.04, 131.69, 131.93, 132.49, 132.75, 134.29, 134.58, 145.97, 148.37, 151.29, 163.94, 164.51; Analalysis Calcd. for C₃₈H₂₄N₂O₂: C, 84.42; H, 4.47; N, 5.18; O, 6.52. Found: C, 84.46; H, 4.40; O, 5.87.

Fabrication of OLED

Prepatterned 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. 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 1 min before being loaded into the vacuum chamber. The organic layers were deposited thermally at a rate of $0.1-0.3 \,\mathrm{nm \, s^{-1}}$ under a pressure of about 10^{-6} torr. The OLEDs devices were constructed with 60 nm of DNTPD as the hole 48/[378]

injection layer, 20 nm of NPD as the hole transporting layer, 20 nm of NBID-1, 2 $(3 \text{ wt}\% \text{ in Alq}_3)$ as the emission layer, 40 nm of Alq₃ as the electron transporting emission layer, 0.5 nm of Al as the cathode. Furthermore, the EL was measured under ambient conditions.

Measurements

The ¹H NMR and ¹³C NMR spectra were recorded with a Bruker AM-200 spectrometer. The FT-IR spectra were measured on a Bomen Michelson series FT-IR spectrometer. The melting points were determined with an Electrothermal Mode 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 calorimeter (DSC) was conducted under nitrogen on a TA instrument 2100 DSC. The sample was heated with 20° C/min from 30°C to 300°C. UV-vis absorption spectra and photoluminescence spectra were measured by Perkin Elmer LAMBDA-900 UV/VIS/IR spectrophotometer and LS-50B luminescence spectrophotometer, respectively. The photoluminescence spectra were reacted on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifer system with a chopping frequency of 150 Hz. Cyclic voltammetry (CV) was performed on an EG and G Parc model 273 A potentiostat/galvanostat nostat system with a three-electrode cell in a solution of Bu₄NBF₄ (0.1 M) in acetonitrile at a scan rate of 100 Mv/S. The polymer films were coated on a square Pt electrode (0.50 cm^2) by dipping the electrode into the corresponding solvents and then drying in air. A Pt wire was used as the counter electrode, and an $Ag/AgNO_3$ (0.1 M) electrode was used as the reference electrode.

Results and Discussion

As shown in Scheme 1, NBID derivatives can be easily synthesized in relatively good yield and it has a non-planar conformation and pushpull structures. Monomer (a) was readily performed in the presence of 4-bromo-1,8-naphthalic anhydride, 1-naphthylamine, isoquinoline, and m-cresol. Finally, NBDI derivatives (1 and 2) were prepared by N-arylation. The NBDI derivatives were examined by spectroscopy analysis. The structure of NBID derivatives identified by ¹H NMR, ¹³C NMR, FT-IR, mass spectrometry, and elemental analysis. The thermal properties of these materials were obtained *via* a thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. 1). The glass-transition temperature (T_g) were observed





SCHEME 1 ■.

at 128°C for NBID-1 and at 148°C for NBID-2, respectively. In addition, the 5% weight loss of NBID derivatives were at 368°C for NBID-1, 407°C for NBID-2, respectively. The high thermal stability indicate that NBID derivatives can form homogeneous and amorphous film through thermal evaporation [15]. UV-vis absorption maximum ($\lambda_{max,UV}$), PL maximum ($\lambda_{max,PL}$), and CV values of NBID derivatives (1, 2) were summarized Table 1. As shown in Figure 2(a, b), Photophysical properties of the NBID derivatives were examined by

	Hexane		Toluene		THF		Dichloro- methane		HOMO/LUMO ^c		AEd	
	$\lambda_{abs}{}^a$	$\lambda_{\rm em}{}^b$	$\lambda_{\rm abs}{}^a$	$\lambda_{\rm em}{}^b$	$\lambda_{\rm abs}{}^a$	$\lambda_{\rm em}{}^b$	$\lambda_{\rm abs}{}^a$	$\lambda_{\rm em}{}^b$	[e	V]	[eV]	
NBID-1 NBID-2	$\begin{array}{c} 442\\ 448\end{array}$	$496 \\ 511$	$\begin{array}{c} 451\\ 456\end{array}$	$\begin{array}{c} 551 \\ 566 \end{array}$	$\begin{array}{c} 450\\ 456\end{array}$	591 610	$\begin{array}{c} 462\\ 467\end{array}$	$\begin{array}{c} 611 \\ 632 \end{array}$	$5.48 \\ 5.46$	$3.06 \\ 3.04$	$2.42 \\ 2.42$	

TABLE 1 Photophysical (in Solution) and Electrochemical (CV) Data of NBID Derivatives (1, 2)

^aAbsorption maximum wavelength (nm).

^bFluorescence maximum wavelength (nm).

^cThe HOMO energy levels were estimated from the onset oxidation potentials, and the LUMO levels were obtained by subtracting the respective optical band-gaps from the HOMO levels.

^dOptical band-gap, calculated from the absorption edge.

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FIGURE 1 TGA and DSC thermograms of NBID derivatives.

UV-vis and fluorescence spectroscopy in solvents of different polarity (hexane, toluene, tetrahydrofuran (THF), and dichloromethane). Red-shift is observed in the solution emission spectrum increases as the solvent polarity, indicating that these molecules possess intramolecular charge transfer from the donor to acceptor unit [16–18]. Electrochemical properties of NBID derivatives were examined by cyclic voltammetry (CV). The LUMO of NBID derivatives were estimated at $-3.06 \,\text{eV}$ (NBID-1) and $-3.04 \,\text{eV}$ (NBID-2), respectively. The HOMO were calculated by the LUMO value and the optical





FIGURE 2 UV-vis absorption and photoluminescence (PL) spectra of NBID derivatives in different solvents. (a): NBID-1 and (b): NBID-2.

band-gap from the edge of the absorption spectrum. CV measurement of NBID derivatives in 0.1 M solution of tetraammonium perchlorate $(Bu_4NClO_4)/acetonitrile$ 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 [20]. The current-density-voltage (J-V), luminance-current-density (L-J),

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FIGURE 3 EL characteristics of the device: ITO/DNTPD (60 nm)/NPD $(20 \text{ nm})/\text{Alq}_3\%$ dopant $(20 \text{ nm})/\text{Alq}_3$ (40 nm)/LiF/Al. (a) EL spectra of NBID derivatives. (b) Voltage-current density. (c) Current density-brightness. (d) Current density-luminous efficiency. (e) Current density-power efficiency.

efficiency-current-density (η -J), and power-efficiency-current-density (η_p -J) characteristic of the device was Figure 3(a–e), respectively. The EL maximum was observed at 574 nm for NBID-1 and at 588 nm for NBID-2, respectively. The Commission International de l'Eclairage (CIE) coordinates of the EL device were found to be (0.46, 0.52) for NBID-1 and (0.48, 0.52) for NBID-2 at 10 mA/cm², respectively. Furthermore, luminance-efficiency were obtained 6.6 cd/A at the voltage of 5.9 V for NBID-1 and 5.9 cd/A at the voltage of 6.3 V for NBID-2, respectively.

CONCLUSIONS

We have synthesized and characterized NBID derivatives as an orange emitting material, where arylamine serves as an electron donor and isoquinoline plays the role of an electron acceptor. NBID derivatives were simply synthesized by *N*-arylation with high yield. NBID derivatives emitted orange light with a peak 574 nm (NBID-1), 588 nm (NBID-2).The CIE coordinates of (0.46, 0.52) for NBID-1 and (0.48, 0.52) for NBID-2 at 10 mA/cm^2 , respectively.

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