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Efficient hole injection material for low operating voltage blue fluorescent organic light emitting diodes

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ABSTRACT

In this paper, we demonstrate a design and synthesis of efficient hole injecting material, 5,10,15-trimethyl-5H-diindolo[3,2-a:3',2'-c] carbazole (TMDI), for blue fluorescent organic light emitting diodes (OLEDs). Our synthesized TMDI material has good hole mobility of about 8.9 x10^{-4} cm^2/Vs and compatible highest occupied molecular orbital level of −5.1 eV, which are important parameters for excellent hole injection layer (HIL) in the OLED applications. The fabricated blue fluorescent OLEDs with TMDI yield about 8% reduction in operating voltage and 39% of improvement in power efficiency as compare to the widely used HIL material 4,4',4"-tris-(N-(naphthalen-2-yl)-N-phenyl-amino) triphenylamine. Such performance enhancements are mainly attributed to good hole mobility of TMDI.

1. Introduction

Since the organic light-emitting diodes (OLEDs) had been developed by Tang and Van Slyke [1], several studies have been carried out to optimize the device architecture from a simple bilayer to much more complicated multilayer structures for their best performances as well as lifetime [2–4]. The performance of OLEDs depend on numerous key parameters such as proper electron and hole injection, efficient charge balance, barrier less contacts and good contact coverage between multilayer etc. Hence, highly efficient OLED devices can be made by properly controlling these parameters and using efficient organic materials. Normally, the work function difference between the electrode and emissive layer creates a significant energy barrier for charge carrier injection, and also makes improper charge balance at the emissive layer, yielding in operating voltage increases and poor device performances [5]. However, the effectual charge injection and transport layers with appropriate highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels between the electrode and emissive layer can improve the charge carrier injection efficiency and light emission of OLEDs. Therefore, the development of effectual organic materials with required optical and electrical characteristics are essential for the progress of OLEDs.

In OLEDs, hole injection layer (HIL) with very deep HOMO level, between indium tin oxide (ITO) electrode and hole transport layer (HTL) has been demonstrated to reduce their driving voltage [6–8]. The efficient HIL materials used in OLEDs generally have intermediate HOMO levels (−5.1 to −5.3 eV) between the work function of ITO (−4.8 eV) and HOMO level of HTL (−5.3 to −5.5 eV) materials [9,10]. Similarly, effective HIL should also provide good contact coverage with ITO anode surface. Furthermore, it should have high transparency in the red, green and blue wavelength region (Eg > 3.0 eV) and high glass transition temperature (Tg) for better thermal stability of OLEDs [11–13]. Copper phthalocyanine (CuPc) [14–16] and few starburst amine type materials such as N,N'-diphenyl-N,N'-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (DNTPD) [17,18], 4,4',4"-tris(N-3-methylphenyl-N-phenyl-amino) triphenylamine (m-MTDATA) [19–22], and 4,4',4"-tris-(N-(naphthalen-2-yl)-N-phenyl-amino) triphenylamine (2-TNATA) [23–25], have been reported for efficient hole injection in OLEDs. The detailed characteristics of these materials are summarized in Table 1.

Among these materials m-MTDATA has poor thermal stabilities due to low Tg values [24] and CuPc is unsuitable for OLED applications due to low transparency in the blue and red region even though CuPc has high hole mobility (2.0×10^{-3} cm^2/Vs) and good thermal stability (Tg: 240 °C) [14].

In this study, we report proficient HIL material, 5,10,15-trimethyl-5H-diindolo[3,2-a:3',2'-c] carbazole (TMDI), which have good mobility, high thermal stability, and excellent transparency for OLED applications. The fabricated blue fluorescent OLED devices with TMDI as HIL show reduction in operating voltage and overall enhancement in the device performances. For the valid comparison of our synthesized TMDI material, commercially available and widely used 2-TNATA and DNTPD materials are used as reference HILs. The electrical and optical properties of TMDI are compared with reference HIL materials.

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Table 1
Comparative values of energy level, Tg, and hole mobility for conventional hole-injecting materials and TMDI.

HILs [References]	CuPc [14–16]	DNTPD [17,20]	m-MTDATA [19–22]	2-TNATA [23–26]	TMDI
HOMO	[a] −5.3	[a] −5.1	[a] −5.1	[a] −5.1	[b] −5.1
LUMO	[a] −3.6	[a] −2.0	[a] −2.0	[a] −2.2	[b] −1.9
Tg (°C)	[a] 240	[a] 106	[a] 75	[a] 110	[b] Not found at DSC
Hole mobility (cm^2/Vs)	[a] 2.0×10^{-3} (TOF)	[b] 8.6×10^{-4} (SCLC)	[a] 6.3×10^{-5} (TOF)	[a] 2.6×10^{-5} (TOF)	[b] 8.9×10^{-4} (SCLC)
Electric field (MV/cm^2)	[a] 0.1	[b] 0.1	[a] 0.63	[a] 0.14	[b] 0.1

[a] Reported value.
[b] Our measured value.

2. Experimental section

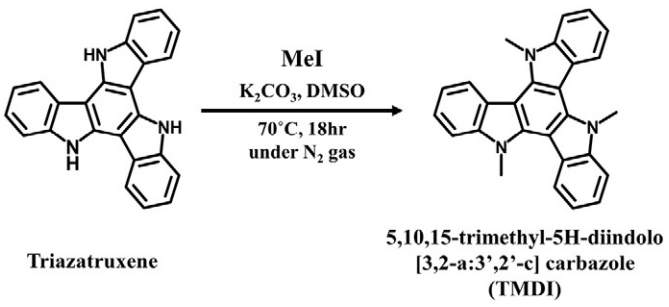
2.1. Materials

All chemicals, reagents, and solvents were purchased from commercial sources and used as received without further purification. All reactions were monitored by thin-layer chromatography with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were measured using Bruker Ultrashied™ 300 in an appropriate solvent solution at 295 K. The ultraviolet-visible (UV–vis) absorption, photoluminescence (PL), and cyclic voltammetry (CV) measurements were obtained by using S-4100 spectrophotometer (JASCO), FP-6500 spectro-fluorometer (JASCO), and EC epsilon electrochemical analysis equipment (BASi), respectively. The elemental analysis was performed on Thermo Fisher Scientific EA-1112. The differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed using Metellor Toledo DSC1 and TA Instrument Q 5000IR, respectively.

2.2. Synthesis of TMDI

The TMDI material was synthesized according to the following process (see Scheme 1). K_2CO_3 (7.20 g, 52.11 mmol) was added to a solution of triazatruxene (3 g, 8.69 mmol), iodomethane (7.40 g, 52.11 mmol) in 60 mL of DMSO under nitrogen. Subsequently, solution was stirred at 70 °C for 18 hours under N_2 atmosphere. After the reaction, the solution was kept for cooling at room temperature and then diluted with water (120 mL) followed by filtering. The residue was purified by column chromatography (EA:Hex = 1:1) to give a white solid. Finally, the obtained solid was re-crystallized in a mixed solution of dichloromethane and methanol to provide a white solid of the product TMDI in 65% isolation yield.

Melting point (MP) 265 °C; decomposition temperature (Td) 388 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 7.99 (d, J = 8.4 Hz, 3H), 7.52 (d, J = 7.6 Hz, 6H), 7.44 (dd, J = 6.4, 7.6 Hz, 6H), 7.36 (dd, J = 7.2, 7.6 Hz, 3H), 7.24 (ddd, J = 10.8 , 7.2, 8 Hz, 6H), 7.01 (dd, J = 7.2, 7.6 Hz, 3H), 6.08 (s, 6H); ^{13}C NMR (400 MHz, $CDCl_3$) 141.9, 139.1, 122.9, 122.8, 121.7, 119.6, 109.6, 102.5, 35.9; HRMS calcd for [$C_{27}H_{21}N_3 + H^+$] 387.1735, found m/z 387.0844



Scheme 1. Synthetic procedure of TMDI.

2.3. Fabrication of device structure

Hole injection materials of 2-TNATA or DNTPD, a hole transporting material of 1,4-bis (1-naphthylphenylamino)-biphenyl (NPB), a fluorescent host of 2-methyl-9,10-di(2-naphthyl)anthracene (MADN), a fluorescent dopant of p-bis(p-N,N-diphenylaminostyryl) benzene (BD-1), and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) electron transport material (ETL) and lithium fluoride (LiF) were purchased from Daejoo Electronic Materials and Gracel (now Dow Chemical company). To fabricate OLEDs, we used a clean glass substrate coated with a 150 nm thick ITO layer having a sheet resistance of 10 Ω/square as an anode. The active area (2×2 mm^2) was patterned by the photolithography and wet etching processes. The glass substrates were cleaned in an acetone and isopropyl alcohol followed by rinsing in deionized water, and finally treated in UV-ozone for 5 min. Each of organic layers was deposited under a vacuum pressure of ~ 10^{-7} Pa with total deposition rate of ~ 0.05 nm/s. Subsequently, 1.5 nm of LiF layer and 100 nm thick aluminum (Al) were deposited in a vacuum chamber without breaking the vacuum and used as a cathode.

2.4 Device characteristics

Current density versus voltage (J-V) and luminance versus voltage (L-V) characteristics of the fabricated OLEDs were measured using Keithley SMU 2635 and Konika Minolta CS-100A. Electroluminescence (EL) spectra and CIE color coordinates were obtained using a Konika Minolta CS-2000A spectroradiometer.

3. Result and discussion

The molecular structure of TMDI is derived from our previously reported hole-transporting material 5,10,15-triphenyl-5H-diindolo[3,2-a:3',2'-c]carbazole (TPDI) [27,28]. TPDI has good hole mobility (6.14×10^{-3} cm^2/Vs) but their deep HOMO level (−5.3 eV) is not suitable for efficient hole injection. Hence, we changed the molecular structure of TPDI by replacing three phenyl units with three methyl units in the molecule and simultaneously their HOMO levels and electron density were compared through density functional theory (DFT) calculation by using Dmol3 module (Material studio, Accelrys software) in which the B3LYP functional was used for the precise computation. Calculated HOMO and LUMO levels of TMDI move to higher levels of about 0.05 and 0.15 eV than the TPDI. This shift in energy levels attributed to the difference of electron density of two molecules in the ground state. As shown in Fig. 1, HOMOs of both molecules are mainly placed in