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1-(*N*-phenylamino)naphthalene oligomers as novel hole transport materials for highly efficient green electrophosphorescence

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ABSTRACT

Two hole transport materials, *N*-(4-carbazol-9-yl-phenyl)-*N*′-naphthalen-1-yl-*N*,*N*′- diphenyl-naphthalene-1,4-diamine and *N*-(4-carbazol-9-yl-phenyl)-*N*′-(4-*N*,*N*- phenyl-naphthalene-naphthalen-1-yl)-*N*,*N*′-diphenyl-naphthalene-1,4-diamine, were synthesized by the addition of a carbazole moiety on to the dimer or trimer of *N*-phenyl-1-naphthylamine. Both of these hole transport materials have high glass transition temperatures of 135 and 167 °C, respectively. The green phosphorescent organic light-emitting diodes (PHOLEDs) of ITO (indium tin oxide)/new hole transport material (50 nm)/Ir(tfmppy)$_2$(tpip) (tfmppy = 4-trifluoromethylphenyl-pyridine, tpip = tetraphenylimidodiphosphinate, 8 wt%): mCP (*N*,*N*′-dicarbazolyl-3,5-benzene, 25 nm)/TmPyPB (1,3,5-trim-pyrid-3-yl-phenyl)benzene, 50 nm)/LiF (1 nm)/Al (100 nm) exhibit high efficiency (maximum current efficiency ($\eta_{c,max}$) of 113.9 and 108.8 cd A^{-1} , maximum external quantum efficiency (EQE) of 29.8% and 28.5%, respectively) with a low efficiency roll-off. At 3000 cd m^{-2} brightness, the η_c values still remain as high as 109.3 and 105.3 cd A^{-1}, respectively. The device performances proved that these new materials derived from *N*-phenyl-1-naphthylamine would be promising hole transport materials for PHOLEDs.

1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have attracted much attention because of their high efficiency and brightness [1–11]. Efficient PHOLEDs generally need balanced charge transport as well as a high conversion efficiency of excitons to light [12–14]. However, a fast reduction of the efficiency (efficiency roll-off) occurs at high luminance, mainly ascribed to the triplet–triplet annihilation (TTA), triplet-polaron quenching (TPQ), or field induced quenching. To overcome this problem, most efficient PHOLEDs tend to have multilayer device configuration with a hole transport layer (HTL), an electron transport layer (ETL) and an emissive layer (EML), and some of them also have a hole injection and an electron injection layer [15–30]. The selection of appropriate materials for each layer is of great importance.

In particular, the hole transport layer plays a key role of determining the device performances. A suitable hole transport material for electrophosphorescence should possess good hole mobility, high glass transition temperature (T_g) to form thermally and morphologically stable thin film, an appropriate highest occupied molecular orbital (HOMO) level to ensure a low energy barrier for hole injection from the anode and then into the EML, a suitable lowest unoccupied molecular orbital (LUMO) level to block electron injection from the EML to the HTL, and a high triplet energy to confine triplet excitons in the EML [15–30]. Additionally, thermal and electrochemical properties of the hole transport layers, the location and extent of the recombination zone, and the presence of charge traps are relevant to the performance of PHOLEDs [31].

Generally, the molecular structures of hole transport materials usually contain electron-donating moieties, such as carbazole, triarylamine, diphenylamine, *N*-phenyl-1-naphthylamine *etc*. Several conventional hole transport materials such as TPD (4,4′-bis[*N*-(*p*-tolyl)-*N*-phenylamino]biphenyl), NPB (*N*,*N*′-di(1-naphthyl)-*N*,*N*′-

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diphenylbenzidine) and TAPC (1-bis[4-[*N*,*N*-di(4-tolyl)amino] phenyl]-cyclohexane) are widely used and they offer many attractive properties such as high hole mobility and ease of sublimation [32–36]. However, due to the high mobility of the hole transport materials, a large number of holes accumulate at the interface of EML and ETL, this causes imbalanced carrier injection. There is still a great demand for the development of hole transport materials with suitable capability that can reduce the injection of holes to counterbalance that of electrons leading to a comparatively higher device efficiency.

In this study, to achieve efficient PHOLEDs, two hole transport materials of *N*-(4-carbazol-9-yl-phenyl)-*N*′-naphthalen-1-yl-*N*,*N*′-diphenyl-naphthalene-1,4-diamine (**CZ-NPNA2**) and *N*-(4-carbazol-9-yl-phenyl)-*N*′-(4-*N*,*N*-phenyl-naphthalene-naphthalen-1-yl)- *N*,*N*′-diphenyl-naphthalene-1,4-diamine (**CZ-NPNA3**) were prepared by the integration of carbazole into the dimer or trimer of *N*-phenyl-1-naphthylamine through the phenyl ring. Ir(tfmppy)$_2$(tpip) (tfmppy = 4-trifluoromethylphenyl pyridine, tpip = tetraphenylimidodi phosphinate) was used as the emitter which has been reported in our former publications with good electroluminescent performances [37–42]. Our results proved that both of the new materials improved the device efficiency with low efficiency roll-off.

2. Experimental section

2.1. General information

All reactions were performed under nitrogen and solvents were carefully dried prior to use. ^{1}H NMR spectra were measured on a Bruker AM 500 spectrometer. Elemental analyses for C, H and N were performed on an Elementar Vario MICRO analyzer. Mass spectra (MS) were obtained with MALDI-TOF (Bruker Daltonic Inc.). TGA and DSC measurements were carried out on STA 449F3 (NETZSCH) and 823e (METTLER), respectively. Crystallographic measurements were carried out using a Bruker SMART CCD diffractometer (Bruker Daltonic Inc.). Absorption and emission spectra were measured on a Shimadzu UV-3100 and a Hitachi F-4600 luminescence spectrophotometer, respectively. The quantum efficiency measurement of **CZ-NPNA2** and **CZ-NPNA3** were measured using 1.0×10^{-5} M quinine in 1 N H_2SO_4 ($\Phi = 0.6$) as the standard in degassed CH_2Cl_2 solution [43]. Cyclic Volta metric experiments were carried out with an IM6ex (Zahner) using three electrode cell assemblies in deaerated CH_2Cl_2 solution with tetrabutylammoniumperchlorate as supporting electrolyte at a scan rate of −100 mV s. Each oxidation potential was calibrated with ferrocene as a reference. PL lifetime measurements were performed by using an excitation line (405 nm) of a laser delivering pulses with 25 ns time duration at 20 Hz repetition rate with Edinburgh FSL-920 spectrophotometer.

2.2. Theoretical calculation

Molecular orbitals were visualized using *GaussView*. The density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were carried out with *Gaussian 09* software package [44]. The geometrical and electronic properties were performed with the *Gaussian 09* program package [45–47]. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functionals) [48] with the 6-31G(d**) atomic basis set. Then the electronic structures were calculated at τ-HCTHhyb/6-311++G (d, p) level [49]. Frontier molecular orbitals were visualized using *GaussView* and their quantified compositions in percentage on different parts were given by *QMForge*. *GaussSum 2.2* was used to broaden the vertical transitions into simulated spectra which was then compared with experimental data through Gaussian distribution with a Full Width at Half-Maximum set (FWHM = 4000 cm^{-1}).

2.3. OLED fabrication and measurement

Organic chemicals used for OLEDs were generally purified by high-vacuum, gradient temperature sublimation. The devices were fabricated by vacuum deposition of the materials at 10^{-6} Torr onto a ITO (indium tin oxide) glass substrate with a sheet resistance of 15 Ω/square with a deposition rate of 1–2 Å/s. The phosphor and mCP host were co-evaporated to form 20 nm emitting layer from two separate sources. The LiF and Al were deposited with deposition rates of 0.1 Å/s and 3 Å/s, respectively. The characteristics of the devices were measured with a computer controlled KEITHLEY 2400 source meter with a calibrated silicon diode in air without device encapsulation. The CIE coordinates were calculated using a testing program of the Spectra scan PR650 spectrophotometer.

2.4. Syntheses procedure

The syntheses procedures of the oligomers of 1-(*N*-phenylamino)naphthalene and **CZ-NPNA2**/**CZ-NPNA3** are shown in Scheme 1.

2.4.1. Syntheses of the intermediates ***NPNA1*** *(N-naphthalen-1-yl-N,N′-diphenyl-naphthalene-1,4- diamine) and* ***NPNA2*** *(N-(4-N,N-phenyl-naphthalene-naphthalen-1-yl)-N,N′-diphenyl-naphthalene-1,4-diamine)*

A mixture of *N*-phenyl-1-naphthylamine (0.88 g, 4.0 mmol), 4,4′-dibromo-2,2'-bipyridine (0.63 g, 2.0 mmol), CuI (0.10 g, 0.50 mmol), 18-Crown-6 (0.05 g, 0.13 mmol), K_2CO_3 (1.11 g, 8.0 mmol) and DMPU (0.15 mL) was placed in a reaction kettle and heated at 240 °C for 5 h under nitrogen. After cooling to room temperature, the mixture was quenched with diluted HCl solution, and then the precipitate was filtered and washed with ammonium hydroxide, water, respectively. The solid was purified with column chromatography on SiO_2 using ethyl acetate and petroleum ether (v: v = 1:10) as eluant to give the intermediates of **NPNA2** (0.15 g, 22%) and **NPNA3** (0.12 g, 21%), successively.

NPNA1: ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.24 − 8.00 (m, 3H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.39 (dt, *J* = 17.3, 4.7 Hz, 3H), 7.33 − 7.18 (m, 5H), 7.15 (t, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.91 (dt, *J* = 23.6, 7.3 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 5.92 (s, 1H). MS (MALDI-TOF, *m/z*): [M]$^+$: Calcd. for $C_{32}H_{24}N_2$:436.194. Found: 436.466. Anal. Calcd. for $C_{32}H_{24}N_2$ (436.55): C 88.04, H 5.54, N 6.42. Found: C 87.94, H 5.61, N 6.35.

NPNA2: ^{1}H NMR (500 MHz, DMSO-d_6, ppm) δ 8.24 (d, *J* = 7.2 Hz, 2H), 8.09 − 7.93 (m, 5H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.54 − 7.34 (m, 7H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.25 − 7.10 (m, 10H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.85 (t, *J* = 7.1 Hz, 1H), 6.84 − 6.79 (m, 2H), 6.60 (t, *J* = 10 Hz, 4H). MS (MALDI-TOF, *m/z*): [M]$^+$: Calcd. for $C_{32}H_{24}N_2$:653.283. Found: 653.523. Anal. Calcd. for $C_{48}H_{35}N_3$ (653.81): C 88.18, H 5.40, N 6.43. Found: C 88.10, H 5.52, N 6.45.

2.4.2. Synthesis of ***CZ-NPNA2*** *and* ***CZ-NPNA3***

Under nitrogen, $Pd(OAc)_2$ (0.02 g, 0.10 mmol), **NPNA2** (0.04 g, 1.0 mmol), Na^{t}BuO (0.38 g, 4.0 mmol), and 1-carbazolyl-4-bromobenzene (0.39 g, 1.2 mmol) were added into a 50 mL two-neck flask. Then, *o*-xylene (20 mL) and P^{t}Bu$_3$ (1.23 mL, 0.4 mmol, 10% in *n*-hexane) were injected. The mixture was heated at 140 °C for 48 h and upon cooling extracted twice with CH_2Cl_2. The organic solution was washed with brine and dried over anhydrous sodium sulfate. The solid obtained was purified with column chromatography on SiO_2 using ethyl acetate and petroleum ether (v: v = 1: 30) as eluant to afford 0.41 g **CZ-NPNA2** (0.60 mmol, 60%). ^{1}H NMR