



Bipolar transport materials for electroluminescence applications



Yi-Wei Tsai ^{a, b}, Jen-Shyang Ni ^a, Feng-Ling Wu ^a, Ming-Chang P. Yeh ^{b, **, *}, Yu-Jen Cheng ^a, Li-Zhong Tsai ^c, Siao-Yin Yu ^c, San-Yu Ting ^c, Li-Yin Chen ^{c, ***, *}, Yuh Sheng Wen ^a, Mandy M. Lee ^a, Jiann T. Lin ^{a, *}

^a Institute of Chemistry, Academia Sinica, Taipei 11529, Taiwan

^b Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan

^c Department of Photonics, National Sun Yat-sen University, Kaohsiung 804, Taiwan

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ABSTRACT

Benzofuranyl benzene incorporating naphthyl (phenothiazinyl or dimesitylboryl) entities via meta-conjugation have been synthesized. These compounds exhibit bipolar transport characteristic with mobilities in the range of 10^{-5} to 10^{-4} cm²/V s at an electric field of 4×10^5 V/cm. The compounds with two naphthyl or dimesitylboryl substituents emit in the violet region with good solution quantum yields. The OLEDs fabricated from the benzofuranyl/dimethylboryl, benzofuranyl/naphthyl and benzofuranyl/dimethylboryl/phenathiazine derivatives have maximum external efficiencies of 1.01%, 1.41% and 3.14%, respectively.

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1. Introduction

Organic light-emitting diodes (OLEDs) continue to be of great interest because of high potential in lighting and display technology. Emitting materials with larger HOMO/LUMO gap, such as blue- or violet emitters, are important for several reasons: (1) they can be used for the prime color of their own in all color display; (2) they can be used as the energy transfer donor for different color emission; (3) violet or blue light laser is useful for information technology. An important component used in OLEDs is the host material for emitting guests, especially when expensive phosphorescent metal complexes are used as the guest. Though bipolar transport is not prerequisite for an emitter, emitters of the type may have some advantages: (1) dispensation with additional hole and electron transport materials is possible; (2) they help with carrying electron and holes to the emitters when used as the host.

In order to have a larger HOMO/LUMO gap, a compound with

extended conjugation should be avoided. Electronic coupling through a *meta*-phenylene bridge (*m*-Ph) is generally weaker than through a *para*-phenylene (*p*-Ph) bridge [1] even though the difference becomes smaller at the excited state [2]. An easy approach for a material to be able to transport electrons and holes is to incorporate entities capable of electron- (ET) and hole-transporting (HT) at the same molecule, though the number of ET and HT entities, and the linkage between them will also affect the overall carrier mobility [3]. We have been interested in bipolar transport materials as the emitter or the host for phosphorescent OLEDs. In addition to be a host, we found these materials may also be used as single-layer OLEDs if they are emitting [4]. Our interest in the materials with large HOMO/LUMO gap leads us to construct *m*-Ph derivatives containing both potential ET and HT entities at mutual *meta*-sites. Benzofuran entity was selected as one of our HT candidates due to the high tendency of benzofuran derivatives to emit in the blue region [5]. Another possible HT candidate is *N*-conjugated 10*H*-phenothiazine entity, an electron donor which can provide large HOMO/LUMO gap when linked to an acceptor via a *m*-Ph unit [6]. For the ET entity, a stable electron deficient dimesitylboryl entity [7], known to be beneficial to electron transport [8] and light emission [9] when incorporated in the conjugated molecules, was chosen. In this paper we will report new *m*-Ph

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: cheyeh@sc.ntnu.edu.tw (M.-C.P. Yeh), ly_chen@mail.nsysu.edu.tw (L.-Y. Chen), jtlin@gate.sinica.edu.tw (J.T. Lin).

derivatives capable of bipolar transport and relevant physical properties including X-ray crystal structures analyses of some compounds.

2. Experimental section

2.1. General information

Unless otherwise specified, all the reactions were carried out under nitrogen atmosphere using standard Schlenk techniques, and the solvents used were purified by standard procedures. All column chromatography was performed with the use of silica gel (230–400 mesh, Macherey–Nagel GmbH & Co.) as stationary phase. The ^1H NMR spectra were recorded on a Bruker AMX400 spectrometer. Electronic absorption spectra were measured in dichloromethane using a Cary 50 Probe UV–visible spectrophotometer. Emission spectra were recorded by a Hitachi F-4500 spectrofluorometer. Emission quantum yields were measured in organic solvents by standard methods [10] with reference to quinine sulfate dehydrate in H_2O ($\phi = 0.56$) [10b] or 9,10-diphenylanthracene in cyclohexane (1.0×10^{-5} M, $\phi = 0.97$). Cyclic voltammetry experiments were performed with a CHI–621B electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a nonaqueous Ag/AgNO_3 reference electrode. The $E_{1/2}$ values were determined as $1/2(E_p^a + E_p^c)$, where E_p^a and E_p^c were the anodic and cathodic peak potentials, respectively. The solvent in all experiments was CH_2Cl_2 and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. DSC measurements were carried out using a Perkin–Elmer 7 series thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$. TGA measurements were performed on a Perkin–Elmer TGA7 thermal analyzer. FAB–mass spectra were collected on a JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan) with a resolution of 8000 (5% valley definition). For FAB–mass spectra, the source accelerating voltage was operated at 10 kV with a Xe gun, using 3-nitrobenzyl alcohol as the matrix. Elementary analyses were performed on a Perkin–Elmer 2400 CHN analyzer. Low-energy photoelectron spectra were taken from a photoelectron spectrometer (AC-2, Riken-Keiki PT5-0210).

2.2. Synthesis

2.2.1. Benzofuran-2-yltributylstannane (**1a**)

To a flask containing benzofuran (1.00 g, 84.6 mmol) in THF (85 mL) prechilled to -78°C was added $n\text{-BuLi}$ (1.6 M in hexane, 3.17 mL, 5.07 mmol) dropwise, and the solution changed color from bright yellow to light orange. After the solution was stirred for 1 h at the same temperature, Bu_3SnCl (2.42 mL, 8.88 mmol) was injected and the solution turned into light brown color. The solution was warmed to room temperature and stirred for 18 h. Aqueous KF was added to quench the excess Bu_3SnCl , and the mixture was extracted with $\text{Et}_2\text{O}/\text{saturated aqueous NH}_4\text{Cl}$ for several times. The collected organic extracts were dehydrated by anhydrous MgSO_4 and filtered through Celite. The filtrate was pumped dry and the residue was purified by column chromatography using hexanes as the eluent. The compound **1a** was isolated as light yellow oil in 99% yield (3.44 g).

2.2.2. 2-(3,5-Dibromophenyl)benzofuran (**1b**)

DMF (0.5 M, 25 mL) was added to a flask loaded with 1,3,5-tribromobenzene (11.6 g, 36.9 mmol), **1a** (5.0 g, 12.3 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (0.26 g, 0.369 mmol), and the dark brown solution was stirred at 80°C for 1 day. After removal of the solvent, the residue was dissolved in CH_2Cl_2 and treated with aqueous KF to

quench **1a**. The mixture was extracted with $\text{Et}_2\text{O}/\text{saturated aqueous NH}_4\text{Cl}$ for several times. The collected organic extracts were dehydrated by anhydrous MgSO_4 and filtered through Celite. The filtrate was pumped dry and the residue was purified by column chromatography using hexanes as the eluent. The compound **1b** was isolated as a white powder in 49% yield. ^1H NMR (acetone- d_6 , 400 MHz): δ 8.11 (br, 2H), 7.77 (s, 1H), 7.69 (d, $J = 7.6$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 1H), 7.55 (s, 1H), 7.39 (pseudo triplet, 1H), 7.30 (pseudo triplet, 1H). ^{13}C NMR (acetone- d_6 , 125 MHz): δ 156.1, 153.3, 135.1, 134.4, 129.9, 127.4, 126.5, 124.5, 122.6, 112.2, 105.4. HRMS (FAB, m/z): $[\text{M}^+]$ calcd for $\text{C}_{14}\text{H}_8\text{Br}_2\text{O}$: 349.8942; found: 348.8948.

2.2.3. 2-(3,5-Di(naphthalene-1-yl)phenyl)benzofuran (**C-naOL**)

To a flask loaded with **1b** (2.24 g, 6.37 mmol), naphthalene-1-ylboronic acid (3.28 g, 19.1 mmol), Na_2CO_3 (2.02 g, 19.1 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.37 g, 0.319 mmol) was added toluene (22 mL). Water (10 mL) and ethanol (5.0 mL) were then added and the solution was heated at 80°C for 18 h. After removal of the solvent, the residue was dissolved in CH_2Cl_2 and filtered through Celite. The filtrate was extracted with $\text{CH}_2\text{Cl}_2/\text{saturated aqueous NH}_4\text{Cl}$ for several times. The collected organic extracts were dehydrated by anhydrous MgSO_4 and filtered. The filtrate was pumped dry and the residue was further purified by column chromatography using hexanes as the eluent. The crude product was recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to provide **C-naOL** as a white powder in 80% yield (2.27 g). ^1H NMR (chloroform- d_1 , 500 MHz): δ 8.14 (d, $J = 7.6$ Hz, 2H), 8.13 (s, 2H), 7.96 (dd, $J = 6.8$; 1.2 Hz, 2H), 7.93 (d, $J = 6.0$ Hz, 2H), 7.68 (s, 1H), 7.62–7.57 (m, 5H), 7.56–7.50 (m, 5H), 7.30 (td, $J = 6.4$; 1.0 Hz, 1H), 7.25 (t, $J = 6.0$ Hz, 1H), 7.11 (s, 1H). ^{13}C NMR (chloroform- d_1 , 125 MHz): δ 155.9, 155.2, 141.7, 139.7, 134.1, 132.1, 131.8, 130.9, 129.4, 128.6, 128.3, 127.3, 126.5, 126.1, 126.1, 125.7, 125.6, 124.7, 123.2, 121.2, 111.4, 102.2. HRMS (FAB, m/z): $[\text{M}^+]$ calcd for $\text{C}_{34}\text{H}_{22}\text{O}$: 446.1671; found: 446.1688. Anal Calcd for $\text{C}_{34}\text{H}_{22}\text{O}$: C, 91.45; H, 4.97. Found: C, 91.17; H, 5.13.

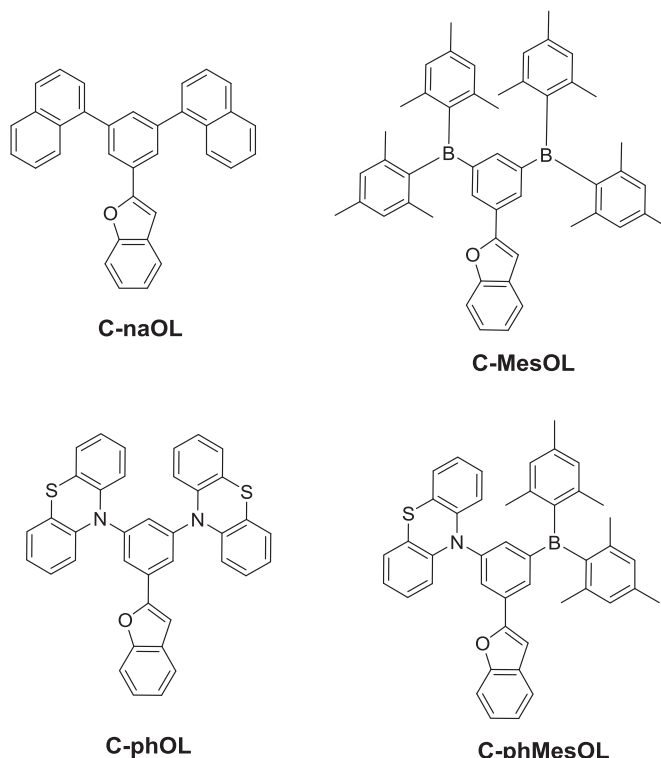


Fig. 1. Molecular structures of the compounds.

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