Bipolar transport materials for electroluminescence applications

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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} cm^2/V s at an electric field of 4 \times 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 10H-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
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 $^1$H NMR spectra were recorded on a Bruker AMX400 spectrometer. Emission spectra were recorded using 3-nitrobenzyl alcohol as the matrix. Elementary analyses were performed by a Perkin-Elmer 2400 CHN analyzer. Low-resolution mass spectra were collected on a JMS-78 fluorometer. Emission quantum yields were measured in a Cary 500 Probe UV—visible spectrophotometer.

2.2. Synthesis

2.2.1. General information

2.2.2. 3-(5-Dibromophenyl)benzofuran (C-naOL)

To a flask containing benzofuran (1.00 g, 84.6 mmol) in THF (85 mL) prechilled to $-78$ °C was added n-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$_3$SnCl (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$_3$SnCl, and the mixture was extracted with Et$_2$O/saturated aqueous NH$_4$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. $^1$H NMR (acetone-d$_6$, 400 MHz): $\delta$ 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 ($\text{pseudo triplet}$, 1H), 7.30 ($\text{pseudo triplet}$, 1H). $^{13}$C NMR (acetone-d$_6$, 125 MHz): $\delta$ 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): [M$^+$] calcd for C$_{14}$H$_8$Br$_2$O: 349.8942; found: 348.8948.

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

To a flask loaded with 1b (2.24 g, 6.37 mmol), naphthalene-1-yloboric acid (3.28 g, 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$_2$Cl$_2$ and filtered through Celite. The filtrate was extracted with CH$_2$Cl$_2$/saturated aqueous NH$_4$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 CH$_2$Cl$_2$/MeOH to provide C-naphthalene as a white powder in 80% yield (2.27 g). $^1$H NMR (chloroform-d$_2$, 500 MHz): $\delta$ 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$_2$, 125 MHz): $\delta$ 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, 125.7, 125.6, 124.7, 123.2, 121.2, 111.4, 102.2. HRMS (FAB, m/z): [M$^+$] calcd for C$_{34}$H$_{22}$O: 446.1671; found: 446.1688. Anal Calcd for C$_{34}$H$_{22}$O: C, 91.45; H, 4.97. Found: C, 91.17; H, 5.13.

2.2.2. 2-(3,5-Dibromophenyl)benzofuran (C-naOL)

To a flask containing 1a (1.60 g, 84.6 mmol), tribromobenzene (11.6 g, 36.9 mmol), 1a (5.0 g, 12.3 mmol) and PdCl$_2$(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$_2$Cl$_2$ and treated with aqueous KF to quench 1a. The mixture was extracted with EtO/saturated aqueous NH$_4$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).
2.2.4. (5-Benzofuran-2-yl)-1,3-phenylene)bis(dimesitylborane) (C-MesOL)

The flask containing a THF solution (10 mL) of 1b (2.55 g, 7.24 mmol) was cooled to \(-78^\circ C\). n-BuLi (2.5 M in hexane, 8.70 mL, 21.7 mmol) was added slowly, and the solution turned into dark red color. After being stirred for 45 min at the same temperature, a THF solution (10 mL) of dimesityl boron fluoride (4.95 g, 22.4 mmol) was added. The solution was slowly warmed to room temperature and stirred for 18 h. After removal of THF by a rotary evaporator, the solution was extracted with CH2Cl2/saturated aqueous NH4Cl for several times. The collected organic extracts were dehydrated by anhydrous MgSO4 and filtered. The filtrate was pumped dry and the residue was further purified by column chromatography using hexanes as the eluent. The residue was further purified by column chromatography using hexanes as the eluent. The crude product was recrystallized from CH2Cl2/MeOH to provide C-MesOL as a white powder in 15% yield (0.60 g).

1H NMR (acetone-\(d_6\), 400 MHz): \(\delta 8.13 (s, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.05 (s, 1H), 6.81 (s, 1H). \)

13C NMR (chloroform-\(d_1\), 100 MHz): \(\delta 156.2, 154.9, 147.0, 143.1, 141.7, 140.7, 138.8, 134.9, 129.8, 129.2, 128.2, 124.1, 122.8, 120.7, 111.3, 101.6, 23.4, 21.2. \)

HRMS (MALDI, \(m/z\)): \([M + Na]^+\) calcd for C50H52B2O, 713.4103; found, 713.4178.

Anal Calcd for C50H52B2O: C, 86.96; H, 7.59; B, 3.13. Found: C, 86.82; H, 7.56.

2.2.5. 10,10'-(5-Benzofuran-2-yl)-1,3-phenylene)bis(10H-phenothiazine) (C-phOL) and 10-(3-benzofuran-2-yl)-5-bromophenyl)-10H-phenothiazine (1c)

The flask loaded with 1b (2.65 g, 7.53 mmol), phenothiazine (0.50 g, 2.51 mmol), sodium tert-butoxide (0.724 g, 7.53 mmol), and a THF solution of 1c (2.65 g, 7.53 mmol) was cooled to \(-78^\circ C\). After being stirred for 45 min at the same temperature, the solution was slowly warmed to room temperature and stirred for 18 h. After removal of THF by a rotary evaporator, the solution was extracted with CH2Cl2/saturated aqueous NH4Cl for several times. The collected organic extracts were dehydrated by anhydrous MgSO4 and filtered. The filtrate was pumped dry and the residue was further purified by column chromatography using hexanes as the eluent. The residue was further purified by column chromatography using hexanes as the eluent.

Table 1: Physical properties of the compounds.

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<th>cpd</th>
<th>(\lambda_{abs,a}) nm</th>
<th>(\lambda_{em,b}) nm</th>
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<th>HOMO/LUMO,e eV</th>
<th>(E_{0-0,f}) eV</th>
<th>(T_g/T_m/T_c/T_d)g (^\circ C)</th>
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<td>355</td>
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<td>1030 (i)</td>
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<td>3.24 (3.29)</td>
<td>110/254/nd/255</td>
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<td>310</td>
<td>508</td>
<td>nd</td>
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<tr>
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<td>nd</td>
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<td>-4.88 (-4.57)/-1.90</td>
<td>2.22 (2.46)</td>
<td>103/235/nd/293</td>
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</table>

a Recorded in CH2Cl2 at 298 K.
b Recorded in toluene solutions.
c Reference for C-naOL: 1.0 \(\times 10^{-5}\) M Quinine sulfate dehydrate in 0.05 M H2SO4(aq) (\(\Phi = 0.56\)); for C-MesOL: 9,10-diphenylanthracene in cyclohexane (1.0 \(\times 10^{-5}\) M, \(\Phi = 0.97\)).
d Measured in CH2Cl2, \(i\): irreversible wave. For C-naOL and C-MesOL, \(E_{m}\) was recorded at the onset point. For C-phOL and C-phMesOL, \(E_{m} = 1/2(\Delta E_{pa} + \Delta E_{pc})\), \(\Delta E_p = E_{pa} - E_{pc}\), where \(E_{pa}\) and \(E_{pc}\) are anodic and cathodic potentials, respectively. All the potentials are reported relative to ferrocene, which was used as the internal standard in each experiment.

The HOMO energies were obtained from theoretical computation, or measured by a low-energy photoelectron spectrometer (in parenthesis), and the LUMO energies were obtained from the computation.

e The HOMO/LUMO gap was calculated by the onset of emission absorption spectra and from computation (in parenthesis).
f HOMO/LUMO gap was calculated by the onset of emission absorption spectra and from computation (in parenthesis).
g \(T_g\): glass transition temperature, \(T_m\): melting point, \(T_c\): crystallization point, \(T_d\): decomposition temperature taken at 5% weight loss. nd: not detected.
Pd(dba)$_2$ (0.057 g, 0.10 mmol) was sequentially added to toluene (25 mL) and tri(tert-butyl)phosphine (0.49 M in toluene, 0.41 mL, 0.20 mmol), and the solution was heated at 80 °C for 18 h. After removal of the solvent, the residue was dissolved in CH$_2$Cl$_2$ and filtered through Celite. The filtrate was extracted with CH$_2$Cl$_2$ saturated aqueous NH$_4$Cl for several times. The collected organic extracts were dehydrated by anhydrous MgSO$_4$ and filtered through Celite. The filtrate was extracted with CH$_2$Cl$_2$ saturated aqueous NH$_4$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 purified by column chromatography using hexanes as the eluent. The crude product obtained was recrystallized from CH$_2$Cl$_2$ cooled MeOH to provide the desired product as a yellow powder in 28% yield (0.33 g).

'1H NMR (acetone-$_d_6$, 400 MHz): δ 8.17 (d, $J = 4.0$ Hz, 2H), 7.65 (d, $J = 7.6$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 1H), 7.42 (s, 1H), 7.33 (m, 1H), 7.25 (m, 1H), 7.05 (d, $J = 7.6$ Hz, 2H), 6.94 (m, 2H), 6.86 (m, 6H), 6.33 (d, $J = 8.0$ Hz, 2H), 2.28 (s, 6H), 2.10 (s, 12H). '

'13C NMR (acetone-$_d_6$, 125 MHz): δ 155.9, 155.5, 154.2, 145.3, 144.1, 135.6, 131.3, 129.9, 128.4, 128.2, 126.7, 126.3, 124.8, 124.3, 123.8, 122.3, 121.0, 117.0, 112.0, 104.2, 23.9, 21.4. HRMS (MALDI, m/z): [M+H]$^+$ Calcld for C$_{38}$H$_{24}$N$_2$O$_2$S, 588.1330; found, 588.1340.

The thermal properties of the compounds were investigated by TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) measurements (Table 1). These compounds possess high thermal decomposition temperatures ($T_d$) ranging from 255 to 338 °C. Except for C-phenOL, all the compounds readily form a glass from ($T_g$) ranging from 78–110 °C when melted on fast cooling and the glassy state persists in the subsequent heating cycles. Compared to other compounds, C-naOL has lower $T_g$ and $T_m$ values, possibly its lower molecular weight and less polar character lead to less intermolecular interaction.

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**3. Results and discussion**

**3.1. Synthesis and thermal properties of the compounds**

New 1,3,5-trisubstituted phenyl derivatives synthesized in this study are shown in Fig. 1. The synthetic route of the compounds is outlined in Scheme 1. Stille C–C coupling reaction [12] between 1,3,5-trisubstituted phenylbenzene and 1/3 equivalent of benzofuran-2-yliyltributylstannane (1a) provides DBBF (1b) in moderate yield. Compound 1b then undergoes Suzuki C–C coupling reaction [13] with naphthalene-1-yloboric acid to afford C-naOL, in contrast, Buchwald-Hartwig C–N coupling reaction [14] of 1b with 1/3 equivalent of phenothiazine gives 1c and C-phenOL in nearly the same yield. Compounds C-MeseOL and C-phMESOL can be obtained from the reaction of dimethyl boron fluoride with lithiated 1b and 1c, respectively.

The thermal properties of the compounds were investigated by TGA (thermogravimetric analysis) and DSC (differential scanning calorimetry) measurements (Table 1). These compounds possess high thermal decomposition temperatures ($T_d$) ranging from 255 to 338 °C. Except for C-phenOL, all the compounds readily form a glass from ($T_g$) ranging from 78–110 °C when melted on fast cooling and the glassy state persists in the subsequent heating cycles. Compared to other compounds, C-naOL has lower $T_g$ and $T_m$ values, possibly its lower molecular weight and less polar character lead to less intermolecular interaction.
3.2. Photophysical properties

The absorption spectra of the compounds in CH$_2$Cl$_2$ are shown in Fig. 2. The band in the range of 275–350 nm is ascribed to the \( \pi \rightarrow \pi^* \) transition and the \( \lambda_{\text{abs}} \) values are very similar among the compounds. The shoulder ranging from 325 to 375 nm is attributed to the intramolecular transfer transition (ICT) which is confirmed by theoretical computation (vide infra). Based on the computational results, the \( S_0 \rightarrow S_n \) \( (n = 1–3) \) transitions of the molecules have very low intensity except for C-naOL. Some transition energies are also comparable for each compound. Consequently, estimation of the HOMO/LUMO gap from the absorption spectra is not unambiguous. We therefore estimate the HOMO/LUMO gap from the onset of the emission at the shorter wavelength side (C-naOL, 3.79 eV; C-MesOL, 3.24 eV; C-phOL, 2.57 eV; C-phMesOL, 2.22 eV: vide infra and Table 1) for our discussions. The wavelength of the ICT band normally increases with a stronger electron acceptor and donor. The order of decreasing ICT band wavelength (from both the emission spectra and theoretical computation), C-phMesOL > C-MesOL > C-phOL > C-naOL, is therefore in accordance with the order of the decreasing donor strength, phenothiazine > naphthyl > benzofuran, and the order of decreasing acceptor strength, dimesitylboryl > benzofuran > naphthyl. The emission spectra (Fig. 2b) of the compounds vary in both intensity and Stokes shift. Compounds C-naOL and C-MesOL have higher quantum yield (C-naOL: 0.80; C-MesOL: 0.33) and less Stokes shift as well as solvatochromic shift (THF vs. CH$_2$Cl$_2$) compared with the other two. This may be attributed to the more orbital overlap (vide infra, see computation) between the ground and excited state of C-naOL and C-MesOL. Energy gap law \[15\] may also accounts for the barely recognizable quantum yields of C-phOL and C-phMesOL. Compounds with arylamine and arylborane at the mutual meta-position of a phenylene linker were also reported to have low quantum yield \[16\]. Dual emission was also found in C-phMesOL. The emission at shorter wavelength (416 nm) is attributed to the \( S_0 \rightarrow S_2 \) transition which is originated from the benzofuran entity to the boran entity. This argument is supported by the PL spectrum of C-phMesOL film measured under excitation wavelength ranging from 260 to 330 nm (260, 275, 280, 290, 300, 310, and 330 nm). The emission at the shorter wavelength can be observed only when the excitation wavelength is shorter than 300 nm (the peak of the short-wavelength emission).
The electrochemical properties of the compounds were studied by cyclic voltammetric methods, and relevant data are shown in Table 1. Reversible oxidation waves were observed for C-phOL and C-phMesOL only, possibly due to the higher stability of the phenothiazine radical cation formed upon oxidation. While there is only one redox wave detected for C-phMesOL (352 mV vs. ferrocene/ferricenium) in THF, it is interesting that C-phOL exhibits two overlapping redox waves. However, the two redox waves can be

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<td></td>
<td>$S_2$</td>
<td>$H_1 \rightarrow L$ (99%)</td>
<td>2.90</td>
<td>429</td>
<td>0.00</td>
<td>$S_2$</td>
<td>$H_1 \rightarrow L_1$ (98%)</td>
<td>3.05</td>
<td>407</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$S_3$</td>
<td>$H_1 \rightarrow L_1$ (8%)</td>
<td>3.40</td>
<td>365</td>
<td>0.00</td>
<td>$S_3$</td>
<td>$H_1 \rightarrow L_1$ (96%)</td>
<td>3.33</td>
<td>373</td>
<td>0.06</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Results are based on gas-phase TD-DFT calculation.

$^b$ $H$ = HOMO, $L$ = LUMO; $H_1$ = The next highest occupied molecular orbital, or HOMO – 1, $H_2$ = HOMO – 2, $L_1$ = LUMO + 1, $L_2$ = LUMO + 2. In parentheses is the population of a pair of MO excitations.

3.3. Electrochemical properties

The electrochemical properties of the compounds were studied by cyclic voltammetric methods, and relevant data are shown in Table 1. Reversible oxidation waves were observed for C-phOL and C-phMesOL only, possibly due to the higher stability of the phenothiazine radical cation formed upon oxidation. While there is only one redox wave detected for C-phMesOL (352 mV vs. ferrocene/ferricenium) in THF, it is interesting that C-phOL exhibits two overlapping redox waves. However, the two redox waves can be
completely resolved to two reversible redox waves (293 and 459 mV vs. ferrocene/ferricenium) in dichloromethane (Fig. S1). This phenomenon strongly suggests that there exists weak electronic interaction between the two phenothiazine entities in $C\text{-phOL}$. The ionization potentials of the compounds in the film state were measured using a low-energy photoelectron spectrometer (AC-2) (Fig. S2). These were then used to estimate the HOMO energy levels of the compounds (Table 1). The stronger donor normally leads to a high-lying HOMO level and a stronger acceptor results in a low-lying LUMO. Accordingly, $C\text{-phOL}$ and $C\text{-phMesOL}$ have upward shift of the HOMO level compared to the other two compounds. The trend of decreasing HOMO levels from AC2 measurement, $C\text{-phOL} > C\text{-MesOL} > C\text{-naOL}$, is therefore in parallel with that observed from the CV data (vide supra). As the estimation of HOMO/LUMO gap from the absorption band edge or the intercept of the absorption and emission spectra is not trivial, we also list the HOMO and LUMO energies and the HOMO/LUMO gap ($E_{0-0}$) obtained from the computation in Table 1 for reference.

3.4. Theoretical computation

Quantum chemistry computation was carried out on the compounds in this study. The computed frontier orbitals of the compounds and their corresponding energy states are included in Fig. 3, and the results for theoretical computation are listed in Table 2. The $S_0 \rightarrow S_1$ transition of $C\text{-naOL}$ has more prominent $\pi \rightarrow \pi^*$ character. In contrast, the $S_0 \rightarrow S_1$ transitions of the other three have prominent ICT character: from benzofuran entity to boron entity in $C\text{-MesOL}$, from phenothiazine entity to benzofuran entity in $C\text{-phOL}$, and from naphthylene entity to boron entity in $C\text{-phMesOL}$.

Table 3
Electron and hole mobilities of compounds measured from the time-of-flight method.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_e \times 10^{-5}$ cm$^2$/Vs</th>
<th>$\mu_h \times 10^{-5}$ cm$^2$/Vs</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-naOL</td>
<td>4.6 (nd)</td>
<td>3.7 (nd)</td>
</tr>
<tr>
<td>C-MesOL</td>
<td>1.8 (d)</td>
<td>1.5 (d)</td>
</tr>
<tr>
<td>C-phOL</td>
<td>19 (nd)</td>
<td>7.5 (d)</td>
</tr>
<tr>
<td>C-phMesOL</td>
<td>36 (nd)</td>
<td>25 (d)</td>
</tr>
</tbody>
</table>

* $\mu_e$: electron mobility.
  * $\mu_h$: hole mobility.

Fig. 4. X-ray structure of the compounds $C\text{-MesOL}$ (a), $C\text{-phOL}$ (b) and $C\text{-phMesOL}$ (c).

Fig. 5. Electron and hole mobilities versus $E^{1/2}$ for films of the compounds.

Table 3
Electron and hole mobilities of compounds measured from the time-of-flight method.

<table>
<thead>
<tr>
<th></th>
<th>$\mu_e \times 10^{-5}$ cm$^2$/Vs</th>
<th>$\mu_h \times 10^{-5}$ cm$^2$/Vs</th>
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<td>4.6 (nd)</td>
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<td>7.5 (d)</td>
</tr>
<tr>
<td>C-phMesOL</td>
<td>36 (nd)</td>
<td>25 (d)</td>
</tr>
</tbody>
</table>

* $d$: dispersive; nd: non-dispersive. The electric field applied: $4 \times 10^5$ V/cm.
respectively. However, the ICT bands have very low oscillator strengths because of the mutual meta-orientation of the donor and the acceptor. The energy of the $S_0 \rightarrow S_1$ transition increases in the order of $\text{C-phMesOL} < \text{C-MesOL} < \text{C-phOL} < \text{C-naOL}$, which is in parallel with the trend of the emission spectra, though the absorption spectra do not account for the conformational relaxation of the Frank Condon excited state.

3.5. Crystal structures

Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol (C-MesOL and C-phOL) or hexane (C-phMesOL) to the dichloromethane solutions of the corresponding complex, respectively. ORTEP plots are displayed in Fig. 4. Selected bond distances and bond angles are collected in Table S1. The bond distances and angles appear to be normal. Two independent molecules exist in the same unit cell for both C-phOL and C-phMesOL, and the two independent molecules have similar conformation except for the dihedral angles between the two phenyl rings belonging to the same phenothiazine unit due to nonplanar nature of the phenothiazine. In C-phOL, the dihedral angles are 31.21 and 7.14° for one and 26.44 and 16.94° for the second molecule, respectively. In C-phMesOL, the dihedral angles for the two molecules are 22.80 and 9.16°, respectively. There is large twist angle between the central phenyl ring and the phenothiazine segment (the best plane formed from the nitrogen atom and the three ipso carbons of the neighboring phenyl rings) for both C-phOL (85.91 and 86.49° for one molecule; 86.45 and 87.24° for the other molecule) and C-phMesOL (80.28 and 83.72°). The twist angle between the benzofuran and the central phenyl ring is small for all the compounds: C-phOL, 2.01 and 8.14°; C-MesOL, 10.21°; C-phMesOL, 5.48 and 5.64°. The boron atom is coplanar with the ipso carbon atoms from the three neighboring phenyl rings, and the mesityl rings are twisted from this plane by 75.93 and 71.67° for one molecule and 75.63 and 67.43° for the other molecule in the lattice of C-phMesOL, and by 73.08 and 67.42° for one boronyl unit and 68.14 and 70.83° for the other boronyl unit in the lattice of C-MesOL. Among the crystal lattices of the three compounds, π-π interaction was found only in C-MesOL. Each molecule forms weak π-π interaction (with a distance of 3.948 Å) with one neighboring molecule via the benzofuran entity. However, such close contact exists only in pairs of molecules and no infinite linkage can be found. Therefore, no solid clue on the carrier mobility (vide infra) can be retrieved from the crystal structural analysis.

3.6. Charge-transport properties

The carrier-transport properties of the compounds were investigated by the time-of-flight (TOF) transient-photocurrent technique at room temperature [17]. The representative TOF transients for electrons and holes of the compounds are shown in Fig. S3 (Supporting Information), and the intersection point of two asymptotes in the double logarithmic representation of these plots are used to calculate the carrier mobilities. All of the compounds exhibit ambipolar carrier-transport behavior, with either dispersive or non-dispersive carrier-transport characteristics. Fig. 5 shows the dependence of the carrier mobilities of various compounds on the electric field, and the carrier mobilities at the electric field of $4 \times 10^4$ V/cm are given in Table 3. The field dependence of carrier mobilities follows the nearly universal Poole-Frenkel relationship: $\mu = \exp(\beta E^{1/2})$, where $\beta$ is the Poole–Frenkel factor [18]. Both hole and electron mobilities of the compounds are in the range of $10^{-4}$ to $10^{-5}$ cm$^2$/V s. The hole mobilities are slightly lower than those ($\sim 10^{-3}$ cm$^2$/V s) of commonly used diphenylamino-based hole-transport materials, N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) [19a] and N,N'-diphenylbenzidine (TPD) [19b]. In contrast, the electron mobilities of the compounds respectively.
are slightly better than those of the typical electron-transport materials, TPBI (\(-10^{-5}\) cm²/(V s)) [20a] and N-arylbenezimidazole-containing analogues (\(-10^{-5} \text{ to } 10^{-6}\) cm²/(V s)) [20b]. All the compounds exhibit comparable electron and hole mobilities, and C-phMesOL containing potent ET (dimesitylborane) and HT (phenothiazine) entities has the highest carrier mobilities among all.

### 3.7. Electroluminescent properties

Among four compounds, C-naOL and C-MesOL are emissive with quantum yields of \(-100\%\) and \(-33\%\), respectively. Due to low glass transition temperature \(T_g\) of C-naOL (78 °C), only C-MesOL was subjected to OLED fabrication. After careful analysis of the HOMO and LUMO energies for the compounds and some relatively available injection/transport materials (Fig. 6), the OLEDs with different configurations were fabricated: device I: ITO (120 nm)/TAPC (30 nm)/TCTA (40 nm)/C-MesOL (30 nm)/TPBi (30 nm)/LiF (0.5 nm)/Al (130 nm), where TAPC (1,1-bis((di-4-tolylamino)phenyl)cyclohexane), TCTA (4,40,400-tris(N-carbonyl)triphenylamine) and TPBi (1,3,5-tris(N-phenylbenzimidazol-2-yl)-benzene) were the hole injection, hole transport and electron transport materials, respectively; device II: ITO (120 nm)/MoO3 (5 nm)/C-naOL (30 nm)/PBD (30 nm)/LiF (0.5 nm)/Al (130 nm), where MoO3 and PBD (2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole) were used as the hole injection and electron transport material; device III: ITO (120 nm)/MoO3 (30 nm)/C-naOL (30 nm)/PBD (30 nm)/LiF (0.5 nm)/Al (130 nm), where TAPC and PBD were used as the hole injection and electron transport materials, respectively. The EL spectrum, \(Ie\), characteristic and efficiency plots are shown in Fig. 7, and the performance parameters are compiled in Table 4. The devices I emits violet light, and the EL spectrum bears close resemblance to the PL spectrum, indicating that light emission is originated from the emitting layer. The device II also emits violet light, and the EL spectrum is slightly red shifted, which may be due to microcavity effect. The

### Table 4

<table>
<thead>
<tr>
<th></th>
<th>C-MesOL</th>
<th>C-naOL</th>
<th>C-phMesOL</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_{on}), V</td>
<td>5.1</td>
<td>3.51</td>
<td>3.4</td>
</tr>
<tr>
<td>(L_{max}), cd/m² (voltage, V)</td>
<td>8719 (12.6); 256 (5.8)</td>
<td>1340 (12)</td>
<td></td>
</tr>
<tr>
<td>(\lambda_{em}, \text{nm})</td>
<td>416</td>
<td>393</td>
<td>579</td>
</tr>
<tr>
<td>CIE (x,y)</td>
<td>(0.1576, 0.0661)</td>
<td>(0.1601, 0.0428)</td>
<td>(0.482, 0.491)</td>
</tr>
<tr>
<td>(\eta_{ext,max}, %)</td>
<td>1.01</td>
<td>1.41</td>
<td>3.14</td>
</tr>
<tr>
<td>(\eta_{max}, \text{lm/W})</td>
<td>0.33</td>
<td>0.22</td>
<td>5.19</td>
</tr>
<tr>
<td>(\eta_{ext,max}, \text{cd/A})</td>
<td>0.55</td>
<td>0.25</td>
<td>7.36</td>
</tr>
<tr>
<td>(\eta_{ext}, 30)</td>
<td>0.40</td>
<td>1.08</td>
<td>1.26</td>
</tr>
<tr>
<td>(\eta_{p}, \text{lm/W})</td>
<td>0.22</td>
<td>0.08</td>
<td>0.99</td>
</tr>
<tr>
<td>(\eta_{c}, \text{cd/A})</td>
<td>0.64</td>
<td>0.12</td>
<td>3.61</td>
</tr>
</tbody>
</table>

\(\eta_{ext,max}\), maximum external quantum efficiency; \(\eta_{max}\), maximum current efficiency; \(L\), luminance; \(\eta_{ext}\), external quantum efficiency; \(\eta_{p}\), power efficiency; \(\eta_{c}\), current efficiency.

\(\eta_{p}\) at a current density of 500 (device I), 100 (device II) or 1000 (device III) cd/m². \(V_{on}\) was obtained from the x-intercept of log(luminance) vs. applied voltage plot.

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performance for the two devices is only mediocre. The non-optimized device exhibited the following performance parameters: I, \( \eta_{\text{ext, max}} = 1.01\% \) at 1 cd/m², \( \eta_{\text{p, max}} = 0.22 \) lm/W, \( \eta_{\text{e, max}} = 0.55 \) cd/A, \( \lambda_{\text{emax}} = 416 \) nm; \( V_{\text{on}} = 5.1 \) V, \( L_{\text{max}} = 8719 \) cd/m²; II, \( \eta_{\text{ext, max}} = 1.41\% \) at 1 cd/m², \( \eta_{\text{p, max}} = 0.22 \) lm/W, \( \eta_{\text{e, max}} = 0.25 \) cd/A, \( \lambda_{\text{emax}} = 393 \) nm, \( V_{\text{on}} = 3.51 \) V, \( L_{\text{max}} = 256 \) cd/m². The device III emits yellow-orange light, and the EL spectrum is similar to the PL spectrum at the longer wavelength region. The absence of the shorter wavelength emission in the EL spectrum (S₂ \( \rightarrow \) S₀ transition, vide supra) may be due to unavailability of the high-lying orbitals at the applied potential. The external quantum efficiency reaches 3.14% despite of very low solution quantum yield of C-phMesOL. Possibly there exists aggregation enhanced emission [21] at the longer wavelength region, Use of C-phMesOL as the host for phosphorescent Ir complex, Ir(pq)₂(acac) [22], was also tested. However, the EL spectrum was the same as that of nondoped device, likely due to inefficient energy transfer between C-phMesOL and Ir(pq)₂(acac).

In addition to full-color light-emitting displays, OLEDs with shorter wavelength emission including UV, violet and deep blue, have potential applications in biological and chemical sensing [23] and information storage [24]. The device performance of the two devices is only mediocre. The non-doped device exhibited the following performance parameters:

- **Photophysical properties**
  - Quantum yield: 1.01% at 1 cd/m²,
  - External quantum efficiency: 1.41% at 1 cd/m²,
  - Luminescence efficiency: 0.22 lm/W,
  - Emission wavelength: 393 nm,
  - Voltage: 3.51 V,
  - Maximum luminance: 256 cd/m².

**References**


**Appendix A. Supplementary data**

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2015.12.026.