Syntheses of Solution-Processable Arylamide Derivatives and Their Application to Organic Light Emitting Devices

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Alkyl-chain substituted arylamine derivatives, solution-processable hole-transporting compounds for organic light-emitting devices (OLEDs), were synthesized. Their thermal, optical, and electrochemical properties were investigated. These compounds exhibited lower melting point than 60 °C and good solubility in common organic solvents, such as toluene, tetrahydrofuran, dichloromethane, and chlorobenzene. The OLEDs with the arylamines as hole-transporting layer from solution-process and tris(8-quinolinolato) aluminum (Alq₃) as emitting layer from dry-process were fabricated. The devices showed comparable driving voltages and improved efficiencies, compared with the corresponding device with N, N'-bis(naphthalen-1-yl)-N, N'-bis(phenyl)benzidine (NPD) as hole-transporting layer from dry-process.

Keyword: arylamine, hole transporting material, solution-process, organic light-emitting device

1. Introduction
Organic light-emitting devices (OLEDs) have attracted a great deal of attention because of their potentials for next generation of flat panel displays and general lighting.[1-2] Solution processes such as slot die coating and ink-jet printing are considered to have an advantage of low cost over the vacuum process for manufacturing of large area displays or lighting, although dry deposition processes under vacuum are far ahead of solution processes from the commercialization point of view. Conjugated polymers have been extensively studied as solution processable materials for OLEDs since 1990.[3] Precise control of molecular weight, end-group structure, and regioregular structure of the conjugated polymers for OLED has been established, but it is not possible to purify structural defects in a polymer chain thoroughly. However, monodisperse small molecules are able to have no structural defects and better purity from conventional purification methods such as column chromatography, recrystallization, and sublimation, and they can also show a good film forming ability.

In hole-transporting materials, N,N'-bis (naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPD) shows high hole mobility and is widely used as a hole-transporting layer in OLEDs.[4] NPD is usually deposited by evaporation process, and its solubility in organic solvents is relatively low. In this report, we synthesized solution-processable NPDs having an alkyl chain, and their solubility in organic solvent, thermal, optical, and electrochemical properties were investigated. The OLEDs with the alkyl-attached NPDs as a hole-transporting layer from solution-process and tris(8-quinolinolato)aluminum (Alq₃) as an emitting layer from dry-process were fabricated. The devices showed comparable driving voltages and improved efficiencies, compared with the corresponding device with NPD from dry-process.

2. Experimental
¹H-NMR and ¹³C-NMR spectra were measured using a JEOL JNM-ECX 400 spectrometer. UV-vis absorption spectra were recorded with a SHIMADZU UV-3150 spectrophotometer. PL spectra were recorded using a Jobin Yvon Fluoromax-4 fluorometer. Thermal transitions were measured on a Perkin-Elmer Diamond DSC (differential scanning calorimeter) and a II EXSTAR 6000 (thermogravimetric analysis) under a nitrogen atmosphere at a heating rate of 10 °C/min. Ionization potentials were measured on a photoelectron yield spectrometer (Sumitomo Heavy Industry PYS).

The OLEDs were fabricated on indium tin oxide
(ITO) coated glass substrates exposed to UV-ozone atmosphere for 20 min. PEDOT: PSS (H. C. Starck AI4083) was spin-coated on ITO. After PEDOT: PSS spin-coated, HTLs were formed by spin-coating at 3000 rpm the corresponding 0.5% HTM dichloroethane solutions on top of PEDOT:PSS and then annealed on a hot plate at 70 °C for 10 min. Under this condition, HTL films with the thickness of 40 nm were obtained. Alq3 was then evaporated on top of the HTL(s). Lithium fluoride (LiF) with the thickness of 0.5 nm and Al with the thickness of 80 nm were evaporated subsequently as cathode. Layer thickness calibration was performed using a Dektak 8 surface profilometer. Current density–voltage characteristics and luminance of the devices were measured on a Keithley 2400 Source Meter and Konica Minolta CS-200 luminance-meter, respectively. The EL spectra were collected using an optical multichannel analyzer (Hamamatsu Photonics PMA-11).

4-(N-(1-Naphthyl)-N-phenylamino)-4′-bromobiphenyl (1): Tris(dibenzylidene acetone)dipalladium (0) (192 mg, 0.210 mmol) and bis(diphenylphosphino)ferrocene (233 mg, 0.420 mmol) were dissolved under N2 atmosphere in 250 mL of dry toluene. The mixture was stirred at ambient temperature for 10 min and then N-phenyl-1-naphthylamine (6.58 g, 30.0 mmol), 4,4′-dibromobiphenyl (31.2 g, 100 mmol), and sodium tert-butoxide (3.46 g, 36.0 mmol) were added to the mixture. The mixture was degassed and placed with N2, and then heated at 100 °C for 7 h. The mixture was allowed to cool to ambient temperature and then the reaction mixture was diluted with toluene and washed twice with water. The organic layer was dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, cyclohexane-toluene (1:0 to 4:1)) to yield 1 (5.60 g, 41%) as white solid. 1H NMR (400MHz, CDCl3): δ 87.94 (d, 1H, J = 8.4 Hz), 7.89 (d, 1H, J = 8.4 Hz), 7.79 (d, 1H, J = 8.0 Hz), 7.53-7.34 (m, 10H), 7.22 (t, 2H, J = 7.9 Hz), 7.13-7.02 (m, 4H), 6.97 (d, 1H, J = 7.3 Hz).

13C NMR (100MHz, CDCl3): δ 148.2, 148.0, 143.2, 139.6, 135.3, 132.6, 131.8, 131.2, 129.2, 128.4, 128.1, 127.4, 127.3, 126.7, 126.5, 126.4, 126.2, 124.2, 122.4, 122.2, 121.4, 120.7. El-MS m/z Caled: 449.1. Found: 449.

N-Phenyl-N,N′-dinaphthylbenzidine (2): Tris(dibenzylidene acetone)dipalladium(0) (38.3 mg, 0.0420 mmol) and bis(diphenylphosphino)ferrocene (46.4 mg, 0.0840 mmol) were dissolved under N2 atmosphere in 60 mL of dry toluene. The mixture was stirred at ambient temperature for 10 min and then 1 (3.77 g, 8.37 mmol), l-naphthylamine (2.99 g, 20.9 mmol), and sodium tert-butoxide (965 mg, 10.0 mmol) were added to the mixture. The mixture was degassed and placed with N2 and then heated at 100 °C for 7 h. The mixture was allowed to cool to ambient temperature and then the reaction mixture was diluted with toluene and washed twice with water. The organic layer was dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, cyclohexane-toluene (1:2)) to yield 2 (3.67 g, 86%) as yellow solid. 1H NMR (400MHz, CDCl3): δ 8.04 (d, 1H, J = 9.2 Hz), 7.96 (d, 1H, J = 8.2 Hz), 7.87 (t, 2H, J = 8.7 Hz), 7.77 (d, 1H, J = 8.3 Hz), 7.59 (s, 1H), 7.53-7.31 (m, 12H), 7.28-7.00 (m, 8H), 6.93 (t, 1H, J = 7.3 Hz), 2.35 (s, 1H). 13C NMR (100MHz, CDCl3): δ 148.4, 147.4, 147.2, 143.5, 135.3, 134.7, 134.0, 134.5, 134.4, 131.3, 129.1, 129.0, 128.6, 128.4, 128.2, 127.6, 127.4, 127.3, 127.1, 126.5, 126.4, 126.3, 126.2, 126.1, 126.0, 125.8, 125.3, 124.3, 122.0, 121.9, 121.8, 121.7, 117.9, 116.4. El-MS m/z Caled: 512.2. Found: 513.

N,N'-Bis(naphthalen-1-yl)-N-phenyl-N'(4-hexyl phenyl)benzidine (HNPD): Tris(dibenzyldiene acetone)dipalladium(0) (38.4 mg, 0.0420 mmol) and tri-tert-butylphosphine (17.0 mg, 0.0840 mmol) were dissolved under N2 atmosphere in 36 mL of dry toluene. The mixture was stirred at ambient temperature for 10 min and then 2 (2.16 g, 4.20 mmol), 1-bromo-4-hexylbenzene (1.02 g, 4.20 mmol), and sodium tert-butoxide (484 mg, 5.14 mmol) were added to the mixture. The mixture was degassed and placed with N2, and then heated at 100 °C for 7 h. The mixture was allowed to cool to ambient temperature and then the reaction mixture was diluted with toluene and washed twice with water. The organic layer was dried over anhydrous magnesium sulfate. After filtration, the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane-toluene (5:1 to 5:2)) to yield HNPD (2.37 g, 83%) as a yellow solid. 1H NMR (400MHz, CDCl3): δ 7.95 (d, 2H, J = 8.0 Hz), 7.88 (d, 1H, J = 8.2 Hz), 7.76 (t, 2H, J = 6.9 Hz) 7.50-7.30 (m, 12H), 7.19 (t, 2H, J = 7.8 Hz), 7.10-6.90 (m, 11H), 2.53 (t, 2H, J = 7.8 Hz), 1.64-1.48 (m, 6H), 0.88 (t, 3H, J = 6.9 Hz). 13C NMR (100MHz, CDCl3): δ 148.5, 147.8, 147.2, 146.0, 143.8, 143.6, 137.0, 135.4, 134.1, 133.2, 131.4, 129.2, 129.2, 128.5, 128.5, 127.4, 127.2, 127.2, 127.1, 126.6, 126.5, 126.5, 126.4, 126.4, 126.3, 126.2, 124.5, 124.4, 122.7, 122.1, 122.0, 121.8, 121.2, 35.6, 31.9, 31.6, 29.2.
22.8, 14.3, El-MS m/z Caled: 672.3. Found: 673.
$\text{N}_2\text{N}^1\text{N}^2\text{bis}(\text{naphthalen-1-yl})\text{-N-phenyl-N'-(4-octylphenyl)}\text{benzidine (ONPD):}$
Tris(dibenzylidene acetone)dipalladium(0) (13.0 mg, 0.0150 mmol) and tri-tert-butylphosphine (6.00 mg, 0.0290 mmol) were dissolved under N$_2$ atmosphere in 12 mL of dry toluene. The mixture was stirred at ambient temperature for 10 min and then 2 (750 mg, 1.46 mmol), 1-bromo-4-octylbenzene (789 mg, 2.93 mmol), and sodium tert-butoxide (168 mg, 1.75 mmol) were added to the mixture. The mixture was degassed and placed under N$_2$, and then heated at 100 °C for 17 h. The further experimental procedure was exactly the same as the synthesis of HNPD, and 800 mg of ONPD (78%) was obtained as a yellow solid. $^1$H NMR (400MHz, CDCl$_3$): $\delta$7.94 (d, 2H, $J = 8.5$ Hz), 7.87 (d, 2H, $J = 8.2$ Hz), 7.75 (t, 2H, $J = 6.9$ Hz), 7.50-7.28 (m, 12H), 7.19 (t, 2H, $J = 7.8$ Hz), 7.10-6.88 (m, 11H), 2.52 (t, 2H, $J = 7.6$ Hz), 1.64-1.48 (m, 2H), 1.38-1.18 (m, 10H), 0.87 (t, 3H, $J = 6.6$ Hz). $^{13}$C NMR (100MHz, CDCl$_3$): $\delta$ 148.5, 147.8, 147.3, 146.0, 143.8, 143.6, 137.0, 135.4, 134.1, 133.2, 131.4, 129.2, 129.2, 128.5, 128.5, 127.4, 127.2, 127.2, 127.2, 126.6, 126.5, 126.5, 126.4, 126.4, 126.3, 126.2, 124.5, 124.4, 122.7, 122.1, 122.0, 121.8, 121.2, 35.5, 32.0, 31.7, 29.6, 29.4, 22.8, 14.3. El-MS m/z Caled: 700.4. Found: 702.

3. Results and Discussion

Synthetic route of the compounds is shown in Figure 1. First, Hartwig-Buchwald palladium-catalyzed C-N coupling of N-phenyl-1-naphthylamine with 4, 4'-dibromobiphenyl gave the compound 1. Compound 2 was also obtained by the C-N coupling with 1-naphthylamine and 1 in the same condition. Finally, the target compounds, hexyl NPD (HNPD) and octyl NPD (ONPD) were obtained by the C-N coupling of 2 with 1-bromo-4-hexylbenzene and 1-bromo-4-octylbenzene, respectively. Only in the third C-N coupling, Bu$_3$P was used as a ligand to enhance the production of a tertiary amylane. The products were purified by silica gel column chromatography and recrystallization, and characterized by $^1$H-NMR, $^{13}$C-NMR, and mass spectroscopy.

The both compounds were highly soluble in common organic solvents, such as toluene, tetrahydrofuran, dichloromethane, and chloro-benzene. Thermogravimetric analysis (TGA) of the compounds showed that they had high thermal stability with 5% weight loss occurred at temperatures ($T_d$) 432 °C for HNPD and 433 °C for ONPD. Differential scanning calorimetry (DSC) of the compounds are shown in Figure 2, and the melting points ($T_m$) were 58 °C for HNPD, and 56 °C for ONPD, which are much lower than 281 °C of unsubstituted NPD. UV-vis absorption and photoluminescence (PL) spectra of the films of HNPD and ONPD on a quartz substrate were measured. All compounds showed almost identical UV-vis and PL spectra, in which absorption maximums were at 347 nm for NPD, and 350 nm for HNPD, and 347 nm for ONPD and emission maximums at 438 nm for NPD, and 440 nm for HNPD, and 439 nm for ONPD.

Ionization potential (Ip) of all compounds, generally corresponding to the energy level of the highest occupied molecular orbital (HOMO), was measured by photoelectron yield spectroscopy (PYS). Electron affinity (Ea), generally corresponding to the energy level of the lowest unoccupied molecular orbital (LUMO), was estimated from the difference between Ip and the optical energy gap (Eg). Both of HNPD and ONPD showed almost same Ip and Ea (Table 1). These results suggest that introducing the alkyl groups into NPD does not affect optical and electrochemical properties. We fabricated the devices with solution-processed (spin-coated) HNPD or ONPD as a HTL and dry-processed (evaporated) NPD as a HTL. The device configuration is the following: ITO / PEDOT: PSS (40 nm) / HTL (40 nm) / Alq$_3$ (60 nm) / LiF (0.5 nm) / Al (80 nm). The PEDOT: PSS was used as a hole-injection layer, and Alq$_3$ was used as a green emitting and electron
transporting layer. The current density–voltage and luminance–voltage characteristics of the devices are shown in Figure 4 and Table 2. The device with HNPD or ONPD showed comparable driving voltages to that of the device with evaporated NPD. This result suggests that the additional alkyl groups to NPD do not deteriorate the hole mobility and hole injection barrier. The efficiencies were 3.7 cd/A, 3.0 lm/W, 1.2 %EQE at 100 cd/m² for HNPD and 3.8 cd/A, 3.0 lm/W, 1.2 %EQE at 100 cd/m² for ONPD. These are even higher than those of the device with evaporated NPD.

Figure 2. DSC thermograms of the HNPD and ONPD.

![Graph showing DSC thermograms of HNPD and ONPD.]

Table 1. Physical Properties of NPD derivatives

<table>
<thead>
<tr>
<th>HTMs</th>
<th>$T_m$ (°C)</th>
<th>$T_d$ (°C)</th>
<th>$\varepsilon_v$ (eV)</th>
<th>$\varepsilon_{et}$ (eV)</th>
<th>$\varepsilon_{ct}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPD</td>
<td>281</td>
<td>434</td>
<td>3.02</td>
<td>5.52</td>
<td>2.50</td>
</tr>
<tr>
<td>HNPD</td>
<td>58</td>
<td>432</td>
<td>2.95</td>
<td>5.51</td>
<td>2.56</td>
</tr>
<tr>
<td>ONPD</td>
<td>153</td>
<td>433</td>
<td>2.95</td>
<td>5.48</td>
<td>2.53</td>
</tr>
</tbody>
</table>

a) Determined by DSC measurement. b) Determined by TGA at 5% weight loss. c) Estimated form onset of UV absorption of the neat film. d) Measured by PYS. e) Calculated with $L$ and $E_{ct}$.

Table 2. Efficiencies at 100 cd/m² and 1000 cd/m² of the devices

<table>
<thead>
<tr>
<th>HTMs</th>
<th>voltage (V)</th>
<th>$\eta_L$ (lm/W)</th>
<th>$\eta_L$ (cd/A)</th>
<th>$\eta_L$ (%)</th>
<th>1000 cd/m²</th>
<th>voltage (V)</th>
<th>$\eta_L$ (lm/W)</th>
<th>$\eta_L$ (cd/A)</th>
<th>$\eta_L$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporated NPD</td>
<td>4.0</td>
<td>2.6</td>
<td>3.3</td>
<td>1.1</td>
<td>5.4</td>
<td>2.2</td>
<td>3.7</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>HNPD</td>
<td>3.9</td>
<td>3.0</td>
<td>3.7</td>
<td>1.2</td>
<td>5.3</td>
<td>2.4</td>
<td>4.1</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>ONPD</td>
<td>4.0</td>
<td>3.0</td>
<td>3.8</td>
<td>1.2</td>
<td>5.5</td>
<td>2.4</td>
<td>4.3</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

$\eta_L$: Luminous efficiency, $\eta_L$: current efficiency, and $\eta_L$: external quantum efficiency.

Figure 3. a) UV-vis and b) PL spectra of HNPD and ONPD.

![Graph showing UV-vis and PL spectra of HNPD and ONPD.]

Figure 4. a) Current density–voltage and b) luminance–voltage plots of the OLEDs with different HTLs.

![Graph showing current density–voltage and luminance–voltage plots of OLEDs with different HTLs.]

Figure 5. Current efficiency–current density plots of the OLEDs with different HTLs.

4 Conclusions

We designed and synthesized the NPD derivatives with alkyl groups for solution-processed OLEDs. The compounds exhibited good solubility in organic solvent. Thermal property and their
solubility were influenced by introducing alkyl groups such as hexyl or octyl, but the optical and electrochemical properties were not influenced. The solution-processed OLEDs with HNPD or ONPD as a hole transporting layer showed comparable driving voltage, and even higher efficiency than those of the device with evaporated NPD.

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References