Phenanthroline Derivatives for Electron-transport Layer in Organic Light-emitting Devices

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A series of novel phenanthroline derivatives (Phens) have been synthesized and their application to organic light-emitting devices (OLEDs) as an electron-transport layer was investigated. The OLEDs with a structure of ITO/α-NPD/Alq_3/Phen/LiF/Al exhibited remarkable performances and lower operating voltages compared to Alq_3-based device, indicating that Phens posses favorable electron-transport properties.

Since Tang et al. reported an organic light-emitting device (OLED) using tris(8-quinolinolato)aluminum(III) (Alq_3) as an electron-transport material (ETM) in 1987,[1] Alq_3 has been widely used. However, devices with Alq_3 generally show higher driving voltage and low efficiency due to its low electron mobility and injection properties.[2] Therefore, the development of ETMs is still necessary for the development of high performance OLEDs. To date, a few materials have been known as electron-transport and injection layers (ETL and EIL) in OLEDs. Among them, bathocuproine (BCP),[3] bathophenanthroline,[4] tetra(2-pyridinyl)pyrazine,[5] 1,3,5-tris(3-methylpyrid-5-yl)triazine,[6] 3,5,3′,5′-tetra(*p*-pyrid-3-yl)phenyl[1,1′]biphenyl[7] have been reported and showed electron-transport and electron-injection properties in OLEDs.

Here, we successfully developed three novel 2-substituted phenanthroline derivatives (Phens) and NPD/Alq_3-based OLEDs using Phens as an ETL. The synthetic route of Phens is shown in Figure 1. First the precursors **2a** and **2b** were prepared via the Suzuki coupling[8] of 3-acetylbenzeneboronic acid and dibromide **1a** and **1b**. Similary, **2c** was prepared from the reaction of 2-acetyl-6-bromopyridine with 1,3-di(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene. 8-Amino-7-quinolinecarbaldehyde (**3**) was obtained in several steps from 7-methylquinoline. The target material Phens were synthesized in 46% yield for Phen1, 64% for Phen2, and 73% for Phen3 respectively according to the literature.[9,10] The compounds were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectrometry, and were purified repeatedly by temperature gradient vacuum sublimation before device fabrication.

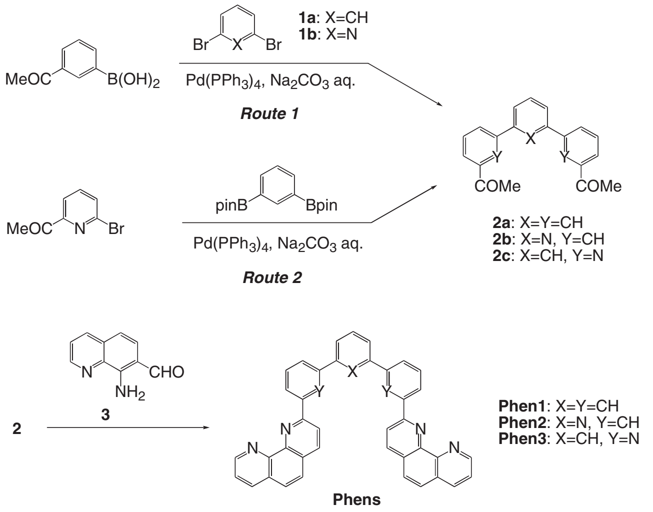

Figure 1. Synthesis of phenanthroline derivatives (Phens).

Table 1. Thermal and electrochemical data of Phens

Compound	T_m/°C[a]	T_d/°C[b]	I_p/eV[c]	E_g/eV[d]	E_a/eV[e]
Phen1	n.d.	489	6.27	3.45	2.82
Phen2	n.d.	493	6.25	3.39	2.86
Phen3	n.d.	475	5.68	3.46	2.22

[a]Determined by DSC measurement. [b]Obtained from TGA analysis. [c]Measured by AC-3 UV photoelectron spectrometer. [d]Taken as the point of intersection of the normalized absorption spectra. [e]Calculated using I_p and E_g values.

The melting points (T_m), decomposition temperatures (T_d), ionization potentials (I_p), electron affinities (E_a), and energy gaps (E_g) of Phens are summarized in Table 1. The glass-transition temperatures (T_g) and T_m of Phens could not be observed, indicating that they form a stable amorphous state. The results of T_d (475–493 °C) exhibit that these phenanthroline derivatives present constant thermal stability. The room-temperature UV–vis absorption (abs) and photoluminescent (PL) spectra of Phens-deposited film on quartz substrates are shown in Figure 2. The absorption edge (λ_{abs}) of Phen1, Phen2, and Phen3 are at 359, 367, and 359 nm and the first PL peaks are at 358, 360, and 355 nm, respectively. According to the absorption edges, the E_g of Phens were estimated to be 3.45, 3.39, and 3.46 eV, respectively.

The electrochemical properties of Phens are very similar to that of BCP. The I_p values of Phen1 and Phen2 were observed at ca. 6.3 eV, which are 0.4 eV deeper than that of Alq_3 (5.9 eV). Thus, hole-blocking properties are expected in OLEDs. Although Phen2 has a pyridine ring in the center of the molecule, the I_p and E_a values of Phen1 and Phen2 are almost the same. Introduction of the pyridine ring does not affect the I_p and E_a values of Phen2. On the other hand, in the case that the pyridine rings are substituted directly to phenanthroline group such as Phen3, shallower I_p and E_a values were observed than that of Phen1 and Phen2. These results clearly show that the position of nitrogen is critically important for tuning the I_p and E_a values of materials.

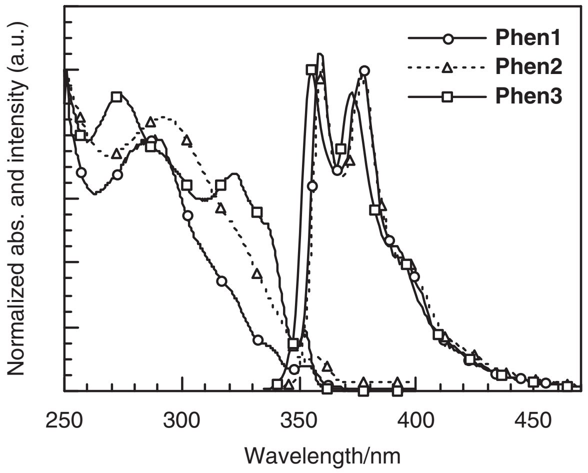

Figure 2. Absorption and photoluminescent spectra of Phens films (50 nm) vacuum deposited on quartz substrate.

To examine the electron-transport properties of Phens, OLEDs with a structure of indium-tin oxide (ITO)/4,4′-*N*,*N*′-bis[*N*-(1-naphthyl)-*N*-phenylamino]biphenyl (α-NPD)/Alq$_3$/Phen/LiF/Al were fabricated. Prior to the fabrication of the organic layers, the ITO substrate was cleaned with ultra-purified water and organic solvents, and treated with an UV–ozone ambient. The hole-transport layer (α-NPD), emission layer (Alq$_3$), and ETL (Alq$_3$ or Phens) were continuously formed on the substrate by vacuum deposition. Finally, a 1-nm-thick LiF layer and 100-nm-thick Al were deposited as the cathode. Current density (J), voltage (V), and luminance (L) characteristics were measured by using a Keithley source meter 2400 and a TOPCON BM-8, respectively.

Figure 3 shows J–V–L characteristics of the devices with Phens or Alq$_3$ as an ETL. The turn-on voltage of devices using Phen1 at 2.7 V and Phen2 at 2.8 V were obviously lower than that with Alq$_3$ at 2.9 V, and Phen1 showed the best performance among these devices. The current densities of devices based on Phen1–3 presented 5.8, 4.0, and 2.3 mA cm^{-2} at 5.0 V, and 424, 324, and 238 mA cm^{-2} at 10.0 V respectively. The increase of nitrogen in Phens tends to reduce the current densities of the device. The Alq$_3$-based device provided current densities of 1.5 mA cm^{-2} at 5.0 V, and 87 mA cm^{-2} at 10.0 V, respectively. High luminance of more than 20000 cd m^{-2} was achieved utilizing Phen1 and Phen2 as an ETL at an applied voltage of 10.0 V. At the same voltage, the Alq$_3$-based device showed about 1/4 lower luminance of 4880 cd m^{-2} than that of Phens. The external quantum efficiency (and the power efficiency) of four devices were recorded at 100 cd m^{-2} to be 1.48% (2.98 lm W^{-1}) for Alq$_3$, 1.47% (3.65 lm W^{-1}) for Phen1, 1.54% (3.66 lm W^{-1}) for Phen2, and 1.29% (2.75 lm W^{-1}) for Phen3, respectively. At 1000 cd m^{-2}, the efficiencies were also recorded to be 1.63% (2.20 lm W^{-1}) for Alq$_3$, 1.65% (2.81 lm W^{-1}) for Phen1, 1.78% (2.90 lm W^{-1}) for Phen2, and 1.53% (2.19 lm W^{-1}) for Phen3, respectively. These results apparently show that electron-transport properties of Phens are much greater than that of traditional electron-transport material, Alq$_3$.

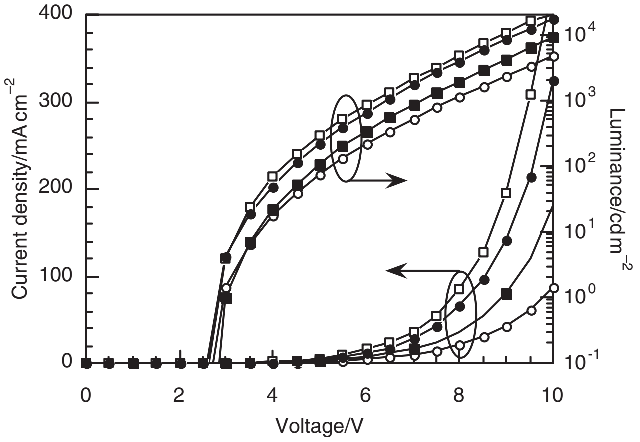

Figure 3. Current density–voltage–luminance characteristics of ITO/α-NPD(50 nm)/Alq$_3$(40 nm)/ETL(30 nm)/LiF/Al, ETL = Alq$_3$ (open circle), Phen1 (open square), Phen2 (closed circle), and Phen3 (closed square).

In summary, a series of novel phenanthroline derivatives were synthesized and their OLED performances as an ETL have been investigated. The Phen-based OLEDs exhibited remarkable performance compared to Alq$_3$ due to favorable electron-transport properties. Further study of Phens for the application to OLEDs is currently in progress.

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References and Notes

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10 A mixture of **2a** (2.1 g, 6.67 mmol), **3** (2.3 g, 13.3 mmol), and saturated ethanolic KOH (1.0 g) in absolute ethanol (20 mL) was heated, and refluxed under nitrogen gas for 24 h. The solvent was evaporated, and the residue was purified by chromatography on silica gel, eluting with CHCl$_3$/EtOAc (1:1), to provide 1.8 g (46%) of Phen1. ^{1}H NMR (CDCl$_3$, 500 MHz), δ 7.62–7.70 (m, 5H), 7.77–7.87 (m, 8H), 8.09 (s, 1H), 8.21 (d, $J = 8.0$ Hz, 2H), 8.27 (d, $J = 8.5$ Hz, 2H), 8.35 (d, $J = 8.0$ Hz, 2H), 8.42 (d, $J = 8.0$ Hz, 2H), 8.55 (s, 2H), 9.22 (d, $J = 4.5$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 120.98, 122.92, 126.35, 126.39, 126.60, 126.86, 127.41, 127.65, 128.41, 129.09, 129.19, 129.35, 136.06, 136.91, 140.39, 141.79, 141.83, 146.19, 146.46, 150.44, 157.70. MS(EI): m/z 587 [M]$^+$.