Highly Efficient Electron-transporting Phenanthroline Derivatives for Electroluminescent Devices

Lixin Xiao,*[1,2] Hsinglin Lan,[3] and Junji Kido*[1,3]
[1]*Optoelectronic Industry and Technology Development Association, 1-20-10 Sekiguchi, Bunkyo-ku, Tokyo 112-0014*
[2]*State Key Laboratory for Artificial Microstructures and Mesoscopic Physics, Department of Physics, Peking University, Beijing 100871, P. R. China*
[3]*Department of Polymer Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa 992-8510*

(Received February 26, 2007; CL-070210; E-mail: kid@yz.yamagata-u.ac.jp, xiao66@pku.edu.cn)

A series of phenanthroline derivatives containing quinoxaline moieties were synthesized, and their electron-transporting properties were investigated by using *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (α-NPD) and tris(8-hydroxyquinolato)aluminum (Alq_3) as the hole-transporting material and the emitting layer, respectively. Higher external quantum efficiency for the phenanthroline derivative than Alq_3 in the electroluminescent devices at a luminance of 100 cd/m^2 was obtained.

A high efficiency for organic light-emitting device (OLED) is a crucial factor to promote the application of OLED in the next generation of flat panel display. The efficiency of OLED is composed of the recombination efficiency of holes and electrons injected from the electrodes to the organic emitting layer and photoluminescence quantum yield of the emitting layer. To improve the efficiency of OLED, the development of highly efficient materials is the major issue, especially the development of highly efficient electron-transporting (ET) materials for OLED. In generally, the mobility of holes in hole-transporting (HT) materials is much higher than that of electrons in ET materials for organic semiconducting materials. Moreover, few materials, mainly bathocuproine[1] and bathophenanthroline (Bphen),[2] oxadiazoles,[3,4] triazoles,[5] 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI),[6] have been used as ET materials for OLEDs. Alq_3[7] is still the most efficient ET materials since the first thin film OLED has been used, although the electron mobility of phenanthroline[8] is faster than that of Alq_3, the prompt crystallization prevents it from a practice. Here, we report a series of highly efficient ET phenanthroline derivatives containing quinoxaline moieties, in which phenanthroline and quinoxaline moieties are coupled to form planar compounds resulting in high electron mobility; moreover, larger groups of fluorene are applied to reduce the crystallization of the phenanthroline derivative.

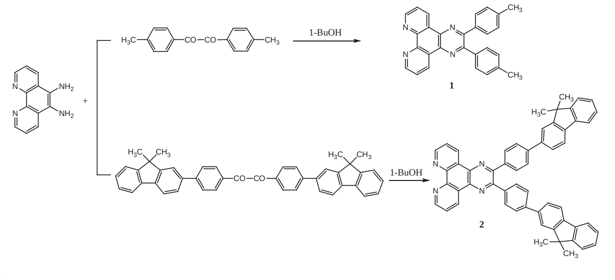
The phenanthroline derivatives were synthesized as shown in Scheme 1 following the reference.[9] 2,3-Di-*p*-tolylpyrazino-[2,3-*f*][1,10]phenanthroline (**1**) and 2,3-bis(4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl)pyrazino[2,3-*f*][1,10]phenanthroline (**2**) were synthesized from 5,6-diamino-1,10-phenanthroline reacting with 1,2-di-*p*-tolylethane-1,2-dione and 1,2-bis(4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl)ethane-1,2-dione,[10] respectively. The purified resultant phenanthroline derivatives by sublimation were identified by ^{1}H NMR and mass spectrometric and elemental analyses.[11]

The absorption spectra of **1** and **2** were measured on films (about 100 nm) that were deposited by high-vacuum (10^{-6} Torr) thermal evaporation on quartz. According to the absorption edge, the energy gap (E_g) of the phenanthroline derivatives can be calculated and listed in Table 1. The lowest unoccupied molecular orbitol (LUMO) energy level of the synthesized phenanthroline derivatives are equal to or lower than that of Alq_3, i.e., the electron affinity (E_a) energy of phenanthroline derivatives might be equal to or higher than that of Alq_3 (3.0 eV). Therefore, it is likely that an equal or higher ET property for the phenanthroline derivative can be obtained than that of the conventional ET material Alq_3.

To study the ET properties of phenanthroline derivatives, OLEDs were fabricated using a 50-nm layer of α-NPD as the HT material, a 40-nm layer of Alq_3 as the emitter. A 30-nm layer of phenanthroline derivatives **1** and **2** as well as Alq_3 (reference device) was then deposited onto the emitter surface as the ET material. Finally, 0.5 nm of LiF together with 100 nm of Al were deposited as the cathode. The device architecture is shown in Figure 1.

The electroluminescence (EL) spectrum of the OLED is shown in Figure 2. An emission peak located at 538 nm is found which is consistent with that of the reference device by using Alq_3 as the ET and the emitter. These indicate that only Alq_3 gives an emission in these devices.

At higher current density than 5 mA/cm^2, higher luminance



Scheme 1. Syntheses of the phenanthroline derivatives **1** and **2**.

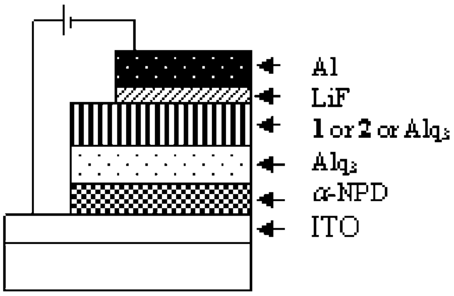


Figure 1. The structure of the OLEDs.

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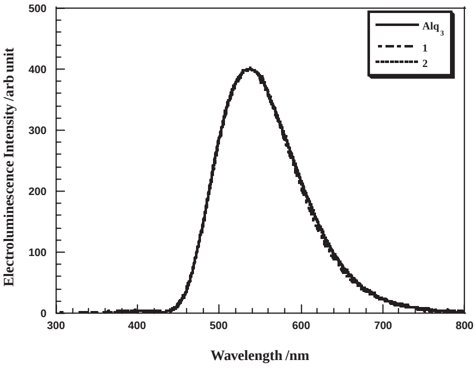

Figure 2. EL spectra of the devices: ITO/α-NPD 50 nm/Alq_3 40 nm/Alq_3 or **1** or **2** 30 nm/LiF/Al.

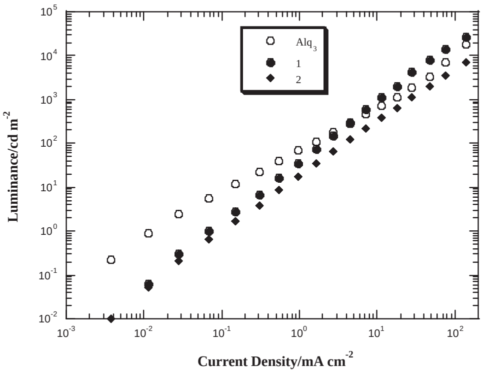

Figure 3. Luminance vs. current density of the devices: ITO/α-NPD 50 nm/Alq_3 40 nm/Alq_3 or **1** or **2** 30 nm/LiF/Al.

of the device using **1** as the ET material was observed under the same current density than that of the reference device (Figure 3). This might be the reason that the ionization potential (I_p) (Table 1) of **1** is lower than that of Alq_3, the holes injected from the emitter and the excitons in the emitter layer might be effectively blocked in the case of **1**. Therefore, the charge balance in compound **1** device might be better than in the Alq_3 device and resulted in a higher current efficiency. This is consistent with higher external quantum efficiency (EQE) for **1** with lower current density at 100 cd/m^2 as shown in Table 2. Although the I_p of **2** is lower enough to block the holes, the electron mobility in **2** might be lower than that in **1** owing to the lower planarity resulting from the larger groups of fluorene to reduce the crystallizability of phenanthroline derivative. This consists with the sublimation experiment, i.e., **1** was more crystallizable than **2**, which can be interpreted by a higher glass-transition temperature (T_g) of 187 °C for **2** than 111 °C for **1** (Table 1), although no obvious crystallization was observed for both **1** and **2** ET films.

An EQE of 1.4% for **1**, which was a little higher than 1.3% for Alq_3, in the OLEDs with 1.9 lm/W of power efficiency (PE) at 100 cd/m^2 was obtained. When the luminance was brighter than 100 cd/m^2, the EQE of **1** was higher than that of Alq_3. For example, 1.8% of EQE for **1** was obtained at 1000 cd/m^2 which was higher than 1.5% for Alq_3. The device performances are listed in Table 2.

Table 1. Properties of the phenanthroline derivatives

ET	I_p/eV	E_a/eV	E_g/eV	T_g/°C
1	6.1	3.0	3.1	111
2	6.2	3.2	3.0	187
Alq_3	5.7	3.0	2.7	175[12]

Table 2. The device performances at 100 cd/m^2

ET	EQE /%	PE /lm·W^{-1}	Current density /mA·cm^{-2}
1	1.4	1.9	2.3
2	0.8	1.0	4.0
Alq_3	1.3	1.9	2.4

In conclusion, a series of phenanthroline derivatives containing quinoxaline moieties were synthesized, and the ET properties were investigated. The phenanthroline derivatives are suitable to be used as ET materials for OLEDs.

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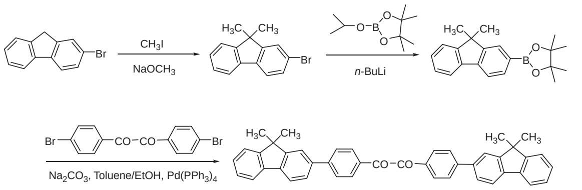
References and Notes

1 G. Parthasarathy, C. Adachi, P. E. Burrows, S. R. Forrest, *Appl. Phys. Lett.* **2000**, *76*, 2128.
2 J. Kido, T. Matsumoto, *Appl. Phys. Lett.* **1998**, *73*, 2866.
3 C. Wang, G.-Y. Jung, Y. Hua, C. Pearson, M. R. Bryce, M. C. Petty, A. S. batsanov, A. E. Goeta, J. A. K. Howard, *Chem. Mater.* **2001**, *13*, 1167.
4 C. Adachi, T. Tsutsui, S. Saito, *Appl. Phys. Lett.* **1989**, *55*, 1489.
5 J. Kido, M. Kimura, K. Nagai, *Science* **1995**, *267*, 1332.
6 J.-P. Duan, P.-P. Sun, C.-H. Cheng, *Adv. Mater.* **2003**, *15*, 224.
7 C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
8 S. Naka, H. Okada, H. Onnagawa, T. Tsusui, *Appl. Phys. Lett.* **2000**, *76*, 197.
9 J. Bolger, A. Gourdon, E. Ishow, J.-P. Launay, *J. Chem. Soc., Chem. Commun.* **1995**, 1799.
10 1,2-Bis(4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl)ethane-1,2-dione was synthesized as the following scheme.



11 **1**: ^{1}H NMR (270 MHz, $CDCl_3$), δ 9.582 (dd, 2H, $J = 6.4$, 1.6 Hz), 9.284 (q, 2H, $J = 2.7$, 2.0 Hz), 7.789 (q, 2H, $J = 4.3$ Hz), 7.622 (d, 4H, $J = 8.0$ Hz), 7.225 (d, 4H, $J = 8.0$ Hz), 2.424 (s, 6H); **2**: ^{1}H NMR (270 MHz, $CDCl_3$), δ 9.639 (dd, 2H, $J = 6.6$, 1.6 Hz), 9.318 (q, 2H, $J = 2.7$, 1.7 Hz), 7.904 (d, 4H, $J = 8.3$ Hz), 7.797 (m, 12H), 7.678 (dd, 2H, $J = 6.3$, 1.7 Hz), 7.471 (q, 2H, $J = 2.7$ Hz), 7.363 (q, 4H, $J = 3.3$ Hz), 1.566 (s, 12H).
12 K. Naito, A. Miura, *J. Phys. Chem.* **1993**, *97*, 6240.

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