doi:10.1246/cl.2010.1222

Published on the web October 20, 2010

Novel Phenanthroline Derivatives for Electron Transport in Organic Light-emitting Diodes

Poopathy Kathirgamanathan,* Sivagnanasundram Surendrakumar, Seenivasagam Ravichandran, Raghava Reddy Vanga,
Juan Antipan-Lara, Subramaniam Ganeshamurugan, Muttulingham Kumaravel, Gnanamoly Paramaswara, and Vincent Arkley
Organic Electronics, Wolfson Centre, Brunel University, Kingston Lane, Uxbridge, UB8 3PH, U.K.

(Received August 24, 2010; CL-100727; E-mail: p.kathir@brunel.ac.uk)

A series of novel arylvinyl-substituted phenanthroline derivatives have been synthesized and their applications as electron-transporting materials in organic light-emitting diodes (OLED's) have been investigated. One particular derivative, namely, 2,9-bis(2-thiophen-2-ylvinyl)[1,10]phenanthroline shows significantly lower operating voltage than tris(8-quinolinolato)aluminum(III) (Alq_3) and substantially higher lifetime than bathophenanthroline (BPhen).

Since Tang et al. reported an organic light-emitting device (OLED) using tris(8-quinolinolato)aluminum(III) (Alq_3) as an electron-transporting material (ETM) in 1987, Alq_3 has widely been employed both in commercial production and research because of its low cost and acceptable lifetime.[1] However, Alq_3 has three disadvantages: (i) Poor mobility, therefore high operating voltage and reduced luminous efficiency, (ii) it leaves behind considerable amount of residue and ash under production condition (during vacuum thermal evaporation), and (iii) perceived toxicological properties of aluminum compounds. Considerable research effort has been expended to develop high mobility materials which would reduce the operating voltage without diminishing the efficiency and lifetime.[2]

In addition to metal quinolinolates, oxadiazole(s), oxazole(s), thiazole(s), imidazole(s), pyridyl compounds, silole(s), perfluorinated oligophenylene(s), phenanthroline(s), and pyrimidone(s) have been reported by several authors.[2–12]

Amongst the phenanthroline derivatives,[2,7] bathophenanthroline (BPhen) and bathocuproine (BCP) have been extensively studied because of their high mobility (1×10^{-4} $cm^2\,V^{-1}\,s^{-1}$) compared to that of Alq_3 (1×10^{-6}–1×10^{-7} $cm^2\,V^{-1}\,s^{-1}$) and deep HOMO levels (typically, −6 to −6.9 eV) which make them excellent hole blockers. However, both virgin BCP and BPhen give significantly poorer lifetime compared to other hole blockers. The former[13–18] tends to crystallize (BCP films crystallize upon storage) and the latter has a very low T_g of 62 °C. Both BCP and BPhen were found to give acceptable lifetime if they are doped or mixed with electron donors such as low work function metals (e.g., Li and Cs) or their complexes.[8–11] Kim and Im[14] reported that their devices with pristine BCP or BPhen lasted only a few hours even at an initial luminance of only 150 cd m^{-2}.

Li et al. recently reported some phenanthroline derivatives with superior performance to Alq_3[9] for their device structure ITO/α-NPB (50 nm)/Alq_3 (40 nm)/ETL (30 nm)/LiF (1 nm)/Al where their best ETM gave a 21% reduction in operating voltage at 1000 cd m^{-2} and 32% increase in power efficiency (lm W^{-1}) compared to Alq_3-based devices. However, no lifetime information was reported.

We have been interested in developing electron transporters cum hole blockers which would give long lifetimes. Here, we report the synthesis of some selected 2,9-substituted phenanthrolines,[20] their physical properties, and their performance as ETM's in green OLED's. The compounds were synthesized according to the general method as shown in Figure 1.

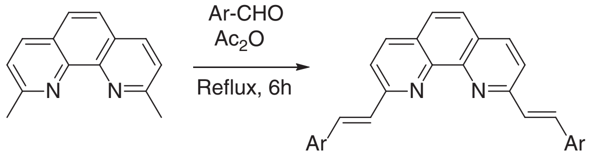

Figure 1. Synthetic scheme for **C-1** (Ar: phenyl), **C-2** (Ar: 4-trifluoromethylphenyl), **C-3** (Ar: 4-cynophenyl), **C-4** (Ar: thienyl).

Table 1. Physcial properties of compounds, **C-1**–**C-4** compared with Alq_3 and BPhen

Comp.	Mp/°C[a]	T_g/°C[a]	T_d/°C[b]	UV, λ_{max} /nm (abs.) Thin Film	FL, λ_{max} /nm (em.) Thin Film
C-1[a]	—[d]	117	—[f]	277, 340 (sh)[g]	453, 493
C-2[b]	279	—[e]	337	279, 345 (sh)[g]	451, 491 (sh)
C-3[a]	289	—[e]	130	313, 362 (sh)[g]	461 (sh), 512
C-4[b]	298	111	345	329, 385 (sh)[g]	520
BPhen[c]	218	62	287	278, 314 (sh)[g]	385, 402 (sh)
Alq_3[b]	415	172	352	265, 393	520

[a]Decomposes on sublimation, so no devices fabricated. [b]Stable in OLED production conditions. [c]Stable in OLED production conditions, but poor lifetime due to low T_g. [d]No mp. [e]No T_g. [f]Not measured. [g]sh: shoulder.

Table 1 summarizes the physical properties of the compounds **C-1**, **C-2**, **C-3**, and **C-4**. All the compounds were purified by double sublimation. Only **C-2** and **C-4** were stable under OLED manufacturing conditions while **C-1** and **C-3** decomposed. The decomposition characteristics were examined under nitrogen atmosphere on a TGA equipment and the compounds **C-2** and **C-4** had high decomposition temperatures (337 and 345 °C respectively) for further device study. HOMO–LUMO levels were determined by cyclic voltammetry (computer-controlled potentiostat PAR 273 or CHI 600D) and band gap measurement from absorption spectroscopy of thin films produced by vacuum thermal evaporation. UV–vis absorption spectroscopy and fluorescent spectroscopy were performed on evaporated thin films on quartz (spectrosil) and are shown in Figure 2. The HOMO–LUMO levels of all the compounds reported in this paper are presented in Figure 3.

Electroluminescent devices were fabricated by vacuum thermal evaporation method using a multichamber OLED pilot plant machine (Solciet, ULVAC, Japan). The devices were fabricated on a patterned (pixilated) ITO substrates (40 Ω/sq, Hitachi High Tech.), cleaned with water, acetone, isopropyl

© 2010 The Chemical Society of Japan

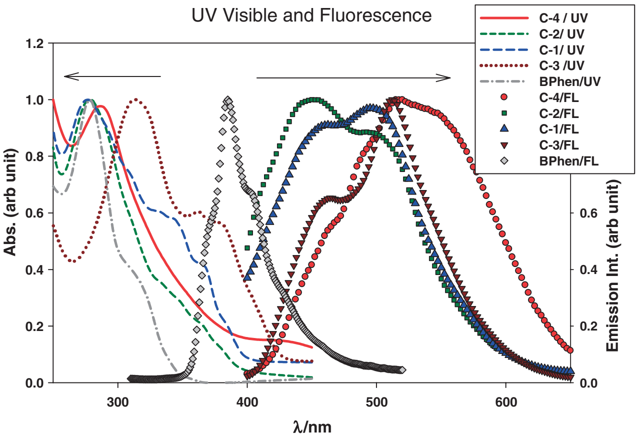

Figure 2. Thin film absorption and fluorescence.

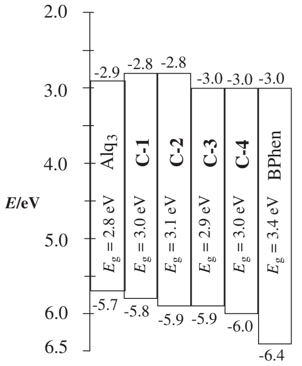

Figure 3. HOMO–LUMO energy levels of **C-1**–**C-4**, Alq_3, and BPhen.

alcohol, and water (in that order), then dried at 150 °C for 20 min and then subjected to ozone cleaning (UV irradiation, 185 nm) at 150 °C for 10 min. The substrates were then plasma cleaned in the presence of oxygen for 25 s and moved into the vacuum chamber from which the hole injector [5,10,15,20-tetra(*p*-tolyl)-21*H*,23*H*-porphine zinc(II) (ZnTPTP)], hole transporter (*N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenylbenzidine (α-NPB)), host (Alq_3):dopant (*N*,*N*′-diphenylquinacridone, DPQA), electron transporter (20 nm) were sequentially deposited at evaporation rates of 0.7, 1.5, 1, 0.002, and 1 $Å\,s^{-1}$ respectively.

An electron injection layer (LiF, 0.5 nm) was deposited on top of the ETM before depositing the top contact (Al, 150 nm).

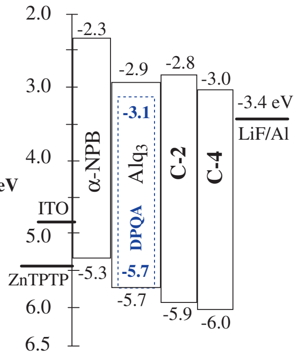

Figure 4. Engery level diagram of OLED device under zero-bias.

All the devices were encapsulated with a UV curable adhesive (Nagase) with glass backplates in a glovebox under nitrogen atmosphere. The electrical and optical measurements were carried out by computer-controlled Keithley 2400 Source Meter and Minolta (CS-1000) spectrometer respectively. Lifetime measurements were carried out on encapsulated devices under constant current density. The employed current density (Column 8, Table 2) was 20 $mA\,cm^{-2}$ for Device D-A (1120 $cd\,m^{-2}$), 10 $mA\,cm^{-2}$ for Device D-**C-2** (972 $cd\,m^{-2}$), and 7 $mA\,cm^{-2}$ for Device D-**C-4** (630 $cd\,m^{-2}$) or 6.4 $mA\,cm^{-2}$ for all the devices (Column 9, Table 2).

All the compounds were found to be fluorescent, light blue as thin films and dark blue in solutions. On substituting the phenyl ring of **C-1** with electron-withdrawing groups such as CF_3 (**C-2**), the HOMO level is depressed by 0.1 eV while LUMO level is unchanged. In contrast, both HOMO and LUMO levels are reduced by 0.1 eV on substituting **C-1** with the CN group (**C-3**). This is consistent with the postulation by Bredas and Heeger.[19] To investigate the electron-transporting characteristics of the compounds **C-2** and **C-4**, we fabricated devices (Figure 4) as follows: ITO/ZnTPTP (50 nm)/α-NPB (50 nm)/Alq_3:DPQA (50 nm: 0.1 nm)/ETL (20 nm)/LiF (0.5 nm)/Al where ETL is Alq_3 or **C-2** or **C-4**. The corresponding devices are assigned D-A, D-**C-2**, and D-**C-4** respectively. Figure 5 shows the current density vs. voltage, luminance vs. voltage plots for Alq_3, **C-2**, and **C-4**. Two important points are immediately apparent. First, the turn-on voltage (to give a luminance of 1 $cd\,m^{-2}$) for devices with **C-4**, **C-2**, and Alq_3 are 3.0, 3.5, and 4.3 V respectively. Second, the operating voltage for the devices with **C-4** is significantly lower than that for the devices with either **C-2** or Alq_3. Devices with **C-2** have slightly

Table 2. Performance of green devices

ETM (Device I.D)	Turn-on voltage/V	V_{op}/V at 1000 $cd\,m^{-2}$	V at 100 $mA\,cm^{-2}$	Eff./$cd\,A^{-1}$ at 1000 $cd\,m^{-2}$	Eff./$lm\,W^{-1}$ at 1000 $cd\,m^{-2}$	Color coordinates CIE (x, y)	Lifetime $t_{1/2}$/h (Initial luminance (L/$cd\,m^{-2}$))[a]	Lifetime $t_{1/2}$/h (Initial luminance (L/$cd\,m^{-2}$))[b]
Alq_3 (D-A)	4.3	11.2	15.0	11.0 ± 0.5	3.0 ± 0.2	(0.325, 0.623)	3384 (1120)	7552 (678)
C-2 (D-**C-2**)	3.5	10.8	16.0	9.0 ± 0.5	2.5 ± 0.2	(0.307, 0.652)	305 (972)	384 (704)
C-4 (D-**C-4**)	3.0	7.1	11.0	10.0 ± 0.5	4.0 ± 0.2	(0.314, 0.647)	3432 (630)	3432 (630)

[a] The current density: 20 (D-A), 10 (D-**C-2**), and 7 $mA\,cm^{-2}$ (D-**C-4**). [b] The current density was 6.4 $mA\,cm^{-2}$ for all the devices.

© 2010 The Chemical Society of Japan

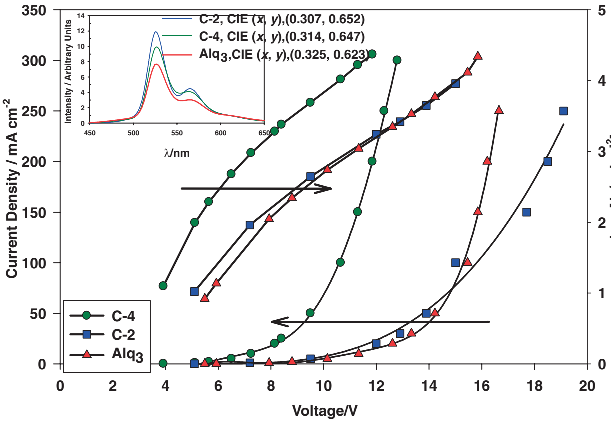

Figure 5. Current density–voltage–luminance characteristics of ITO/ZnTPTP (50 nm)/α-NPB (50 nm)/Alq_3:DPQA (50 nm:0.1 nm)/ETL (20 nm)/LiF (0.5 nm)/Al.

lower operating voltage than Alq_3-based devices in the low voltage region, though the trend is reversed at higher voltages ($V > 13$ V). For example, at 1000 cd m^{-2}, the devices with **C-4** have 23% lower operating voltage compared to the devices with Alq_3. The power efficiency (lm W^{-1}) for devices with **C-4** is 43% higher than that with Alq_3, but the current efficiency is comparable (Table 2). Devices with **C-2** have lower power efficiency and current efficiency than devices with Alq_3. The above observation can be explained on the basis of higher mobility of **C-4** (lower operating voltage and turn-on voltage) compared Alq_3 and the barrier height for the electron injection is lowest for **C-4** (0.4 eV), then Alq_3 (0.5 eV) and highest for **C-2** (0.6 eV). However, the turn-on voltage does not follow the barrier height. The turn-on voltage follows the order: **C-4** < **C-2** < Alq_3. This can be explained on the basis of mobility differences inferred from the color coordinates of the electroluminescent spectra (Figure 5, inset and Table 2).

The CIE color coordinates (x, y) for devices with **C-2** are more saturated green than devices with either **C-4** or Alq_3. The more saturated the green color, the closer the emission is to the hole transporter, α-NPB (interface) and in turn, higher mobility of the compound in question. Further, the observed color coordinates are consistent with the relative HOMO levels (i.e., hole blocking nature) of the ETM's concerned. The HOMO levels of **C-4**, **C-2**, and Alq_3 are −6.0, −5.9, and −5.7 eV respectively and the hole blocking ability is expected to be in the same order. Lifetime of the devices was measured under constant current driving. Devices with Alq_3 as ETM (D-A) have half-life of 3384 h (Initial luminance = 1120 cd m^{-2}) and 7552 h (Initial luminance = 678 cd m^{-2}) whereas the ones with **C-4** (Device D-**C-4**) have a lifetime of 3432 h (Initial luminance = 630 cd m^{-2}) and **C-2** (D-**C-2**) have a lifetime of only 384 h at initial luminance of 704 cd m^{-2}. Though the lifetime of the devices with **C-4** is lower than that with Alq_3, it is still 1000-fold higher than corresponding devices with pristine BPhen as ETM whose lifetime is only a few hours (the devices degrade within hours of manufacture). Further work is on going in understanding the mechanism of conduction of the devices based on **C-2** and **C-4** and their performance in blue devices where the ETM's (**C-2** and **C-4**) are both employed as virgin and doped. This will be published elsewhere. Although compound **C-3** is not evaporable under vacuum, its potential as a solution processed ETM is under investigation. We have demonstrated that it is possible to produce phenanthroline derivatives (example, **C-4**: 2,9-bis-[2-(thiophen-2-yl)vinyl][1,10]phenanthroline) which can act as good electron transporters and hole blockers with reasonably long lifetimes even in their virgin form.

References and Notes

1 C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913.
2 D. Tanaka, T. Takeda, T. Chiba, S. Watanabe, J. Kido, *Chem. Lett.* **2007**, *36*, 262.
3 H. Sasabe, T. Chiba, S.-J. Su, Y.-J. Pu, K. Nakayama, J. Kido, *Chem. Commun.* **2008**, 5821.
4 M. Ichikawa, N. Hiramatsu, N. Yokoyama, T. Miki, S. Narita, T. Koyama, Y. Taniguchi, *Phys. Status Solidi RRL* **2007**, *1*, R37.
5 P. Kathirgamanathan, WO 00/32717, **2000**.
6 T. Sano, M. Fujita, T. Fujii, Y. Nishio, Y. Hamada, U.S. Patent 5456988, **1995**.
7 A. P. Kulkarni, C. J. Tonzola, A. Babel, S. A. Jenekhe, *Chem. Mater.* **2004**, *16*, 4556.
8 S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem, K. Leo, *Nature* **2009**, *459*, 234.
9 Y.-J. Li, H. Sasabe, S.-J. Su, D. Tanaka, T. Takeda, Y.-J. Pu, J. Kido, *Chem. Lett.* **2009**, *38*, 712.
10 S. R. Forrest, V. Bulovic, P. Peumans, U.S. Patent 6,451,415, B1, **2002**.
11 H.-W. Lee, J.-G. An, H.-K. Yoon, H. Jang, N. G. Kim, Y. Do, *Bull. Korean Chem. Soc.* **2005**, *26*, 1569.
12 P. Kathirgamanathan, S. Surendrakumar, PCT Patent WO 078115 A1, **2008**.
13 P. Kathirgamanathan, V. Arkley, S. Surendrakumar, Y. F. Chan, S. Ravichandran, S. Ganeshamurugan, M. Kumaraverl, J. Antipan-Lara, G. Paramaswara, V. R. Reddy, *SID Symp. Dig.* **2010**, *41*, 465.
14 Y. Kim, W. B. Im, *Phys. Status Solidi A* **2004**, *201*, 2148.
15 C.-H. Hsiao, S.-W. Liu, C.-T. Chen, J.-H. Lee, *Org. Electron.* **2010**, *11*, 1500.
16 S. Naka, H. Okada, H. Onnagawa, T. Tsutsui, *Appl. Phys. Lett.* **2000**, *76*, 197.
17 K. Okumoto, H. Kanno, U.S. Patent 0051563A1, **2006**.
18 J. P. Chen, X. C. C. Li, U.S. Patent 6,713,781,B1, **2009**.
19 J. L. Brédas, A. J. Heeger, *Chem. Phys. Lett.* **1994**, *217*, 507.
20 A mixture of neocuproine hydrate (24 mmol) and aryl aldehyde (50 mmol) was refluxed in acetic anhydride (20 mL) for 6 h and then allowed to cool for 18 h. To the reaction mixture which contained the product as solid, methanol and small amounts of water were added (50:2). The product was filtered off under suction then washed thoroughly with methanol, water, diethyl ether and dried under vacuum at 80 °C for several hours. The product was purified by sublimation (at 10^{-6}–10^{-7} Torr) to give an analytically pure material.

2,9-Bisstyryl[1,10]phenanthroline (C-1): No melting peak was obtained on DSC, T_g 117 °C. Anal. Found: C, 87.35; H, 5.18; N, 7.43%. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.28%.

2,9-Bis(4,4′-trifluoromethylphenyl)vinyl[1,10]phenanthroline (C-2): Obtained as a light yellow solid, mp 279 °C (DSC, onset); Anal. Found: C, 69.54; H, 3.39; N, 5.40%. Calcd for $C_{30}H_{18}N_2F_6$: C, 69.23; H, 3.49; N, 5.38%. ^{1}H NMR (DMF-d_6): δ 7.88 (d, $J = 8$ Hz, H-2, 2H), 7.93 (d, $J = 16$ Hz, H-4), 8.02 (s, H-8), 8.03 (s, H-7), 8.11 (d, $J = 8$ Hz, H-1, 2H), 8.20 (d, $J = 8.3$ Hz, H-5), 8.26 (d, $J = 16$ Hz, H-3), 8.58 (d, $J = 8.3$ Hz, H-6).

2,9-Bis(4,4′-cyanophenyl)vinyl[1,10]phenanthroline (C-3): Mp 289 °C (DSC, onset). Anal. Found: C, 82.67; H, 4.07; N, 12.82%. Calcd for $C_{30}H_{18}N_4$: C, 82.93; H, 4.18; N, 12.89%.

2,9-Bis[2-(thiophen-2-yl)vinyl][1,10]phenanthroline (C-4): Obtained as a golden yellow solid, mp 298 °C (DSC, onset); T_g 111 °C. Anal. Found: C, 72.85; H, 4.12; N, 7.10; S, 16.17%. Calcd for $C_{24}H_{16}N_2S_2$: C, 72.70; H, 4.07; N, 7.06; S, 16.17%. ^{1}H NMR (DMF-d_6): δ 7.21 (dd, H-3), 7.45 (d, $J = 16$ Hz, H-7), 7.52 (d, $J = 3.5$ Hz, H-4), 7.67 (d, $J = 5$ Hz, H-2), 7.95 (s, H-10, 11), 8.15 (d, $J = 8.3$ Hz, H-8), 8.32 (d, $J = 16$ Hz, H-6), 8.49 (d, $J = 8.3$ Hz, H-9).

Those Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

© 2010 The Chemical Society of Japan