

Arylvinylene phenanthroline derivatives for electron transport in blue organic light emitting diodes

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ABSTRACT

A series of novel arylvinylene substituted phenanthroline derivatives has been synthesised and their application as electron transporting materials in organic light emitting diodes (OLEDs) has been investigated. One particular derivative, namely, 2,9-bis-(2-thiophen-2-yl-vinyl)-[1,10]phenanthroline (C-4) shows significantly lower operating voltage (36% reduction) and increase of power efficiency of up to 83% compared to tris (8-quinolinolato)aluminium (III) (Alq₃). C4 also shows substantially longer (nearly 6-fold) life-time than bathophenanthroline (BPhen) in blue devices. Doping of C4 with electron donors such as m-MTDATA, α -NPB and lithium quinolinolate (Liq) further reduces the turn-on voltage and operating voltage.

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1. Introduction

Organic light emitting diode (OLED) based displays have become one of the significant flat panel display technologies as evidenced by the production of active matrix OLEDs for mobile phones by Samsung SDI and the introduction of 11" AM-OLED TV (XEL-1) to the market by Sony. Recent announcement by Samsung of its intention to invest US Dollars 2.2 billion into active matrix OLED Television (AM-OLED) to bring them into mainstream TV market has given considerable impetus to the scientists developing materials for the OLED devices [1–9].

Since Tang et al. reported an organic light emitting device (OLED) using tris (8-quinolinolato)aluminium (III) (Alq₃) as an electron transporting material (ETM) in 1987, Alq₃ has widely been employed both in commercial production and research because of its low cost and acceptable life-time [2]. However, Alq₃ 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). (iii) Perceived toxicological properties of aluminium compounds. Considerable research effort has been expended to develop high mobility materials which would reduce the operating voltage without diminishing the efficiency and life-time [8,9]. In addition to metal quinolates, oxadiazole(s), oxazole(s), thiazole(s), imidazole(s), pyridyl compounds, silole(s), perfluorinated oligophenylene(s), phenanthroline(s), pyrimidone(s) and triazine(s) have been reported by several authors [3–8,10–14,19,28–31].

Amongst the phenanthroline derivatives, bathophenanthroline (BPhen), bathocuproine (BCP) have been extensively studied because of their high mobility ($1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) compared to that of Alq₃ ($1 \times 10^{-6} \text{--} 1 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [6–7] and deep HOMO levels (typically, -6 eV to -6.9 eV) which make them excellent hole blockers. However, both virgin BCP and BPhen give significantly poorer life time compared to other hole blockers. The former tends to crystallize (BCP films crystallize upon

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storage) and the latter has a very low T_g of 62 °C [9,15–17]. 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 [10–13]. Kim and Im [15] reported that their devices with pristine BCP or BPhen lasted only a few hours even at an initial luminance of 150 cd m⁻². Another potential candidate, 1,3,5-tris(phenyl-2-benzimidazolyl)benzene (TPBI), has similar crystallisation problem [21].

Yan-Jun Li et al. recently reported some phenanthroline derivatives with superior performance to Alq₃ [11] for their device structure ITO/ α -NPB (50 nm)/Alq₃ (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) compared to Alq₃ based devices. However, no life-time information was reported.

A good electron transporter (et) should have the following characteristics [7]: (i) high electron affinity to match with the workfunction (W.F.) of the cathode, thus reducing the energy barrier; (ii) high electron mobility ($\mu_e > 1 \times 10^{-5}$ cm² V⁻¹ s⁻¹) to aid the transport of electrons into the emissive layer and efficiently confine the excitons in this layer; (iii) a reversible electrochemical reduction with a sufficiently high reduction potential; (iv) a high ionisation potential (I.P.) to serve as a hole blocker (I.P. > 6 eV); (v) a high glass transition temperature and melting point; (vi) thermal stability up to at least 250 °C (high $T_g/T_m/T_d$); (vii) stability under evaporation conditions for a period of at least

144 h if vacuum processing is employed as the manufacturers would like to run their production equipment at least for 6 days in a row without interruption; (viii) good stability to moisture and oxygen; (ix) capable of forming amorphous film so that crystallisation induced degradation is avoided; (x) photostability; (xi) if phosphorescent emitters are used, the triplet energy level of the et should be higher than that of the phosphorescent emitters; (xii) processability to produce uniform and pinhole-free films either by evaporation (small molecules) or by solution casting.

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, their physical properties and their performance as ETMs in blue OLEDs [14].

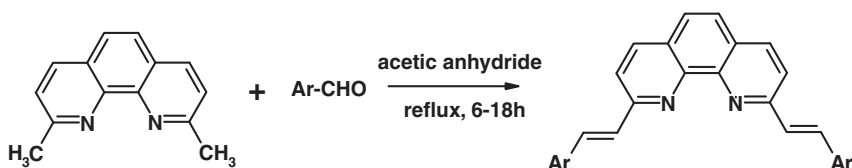
2. Experimental

2.1. Synthesis

The compounds were synthesized according to the general method as shown in Scheme 1. All the compounds were purified by double sublimation.

2.1.1. 2,9-Bis(styryl)-[1,10]-phenanthroline [C-1]

A mixture of neocuproine hydrate (5.0 g; 0.024 mol) and benzaldehyde (5.4 g; 5.2 mL; 0.050 mol) was refluxed



Scheme 1. Ar = phenyl (C-1), 4-trifluoromethylphenyl (C-2), 4-cyanophenyl (C-3) and thienyl (C-4).

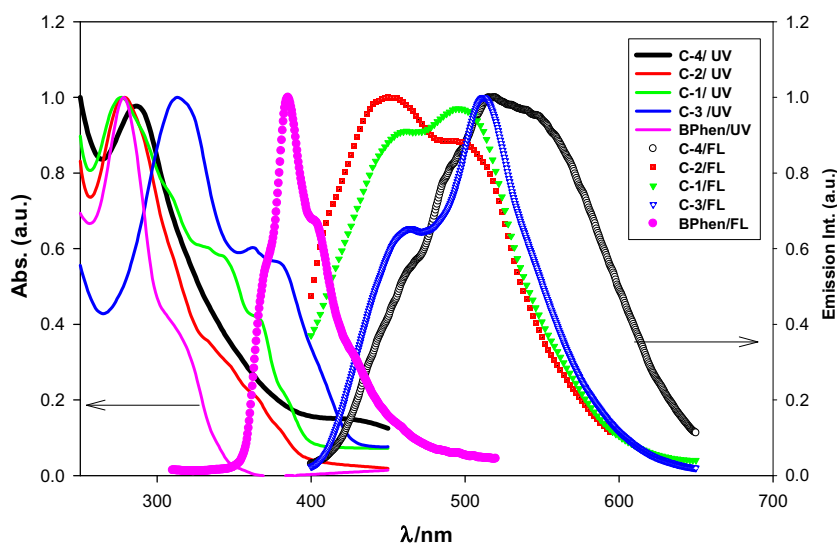


Fig. 1. Thin film UV-Vis absorption and fluorescence spectra of C-1, C-2, C-3, C-4 and BPhen. Excitation wavelengths: C-1 (360 nm), C-2 (360 nm), C-3 (350 nm), C-4 (350 nm) and BPhen (350 nm).

in acetic anhydride (20 mL) for 6 h and the cooled reaction mixture was poured into ice-cold water. The product was extracted into ethyl acetate. The organic phase was washed with water, dried over anhydrous magnesium sulphate and then the solvent removed. To the residue con. HCl was added and the yellow solid that obtained was again taken into dichloromethane and extracted with 5% NaOH solution. The organic phase was washed well with water, dried over anhydrous magnesium sulphate and solvent removed to give a yellow solid. The product was purified by column chromatography on silica gel (eluent: CH_2Cl_2 –MeOH 49:1). The eluents containing the product was evaporated and by addition of ether and petroleum ether gave an analytically pure material 4.8 g (52%). *Anal.* Calc. for $\text{C}_{28}\text{H}_{20}\text{N}_2$: C, 87.47; H, 5.24; N, 7.28. Found: C, 87.14; H, 5.15; N, 7.20%. ^1H NMR (CDCl_3): 7.33(t, $J = 7.4$ Hz, H-1), 7.42(t, $J = 7.4$ Hz, H-2), 7.70(d, $J = 8.3$ Hz, H-3), 7.78(d, $J = 16$ Hz, H-4), 7.73(d, $J = 16$ Hz, H-5), 7.89(d, $J = 8.4$ Hz, H-6), 8.16(d, $J = 8.4$ Hz, H-8), 7.68 (s, H-8 and H-9).

2.1.2. 2,9-Bis(4,4'-trifluoromethylphenyl)vinyl-[1,10]-phenanthroline [C-2]

A mixture of neocuproine hydrate (5.0 g; 0.024 mol) and 4-(trifluoromethyl)benzaldehyde (8.8 g; 0.050 mol) was refluxed in acetic anhydride (20 mL) for 6 h and then allowed to cool for 18 h to give light pinkish crystals. Methanol and small amounts of water were added and the crystals were collected by suction filtration. The product was then washed thoroughly with methanol, water and diethyl ether before dried under vacuum at 80 °C for several hours to give (7.9 g; 63%) of product. Finally, the product was purified by sublimation (270 °C at 10^{-6} Torr) to give an analytically pure material as a light yellow solid, m.p. 279 °C (DSC, onset); 285 °C (DSC, peak). *Anal.* Calc. for $\text{C}_{30}\text{H}_{18}\text{N}_2\text{F}_6$: C, 69.23, H, 3.49; N, 5.38. Found: C, 69.54, H, 3.39, N, 5.40%; ^1H NMR (d-DMF): 7.88(d, $J = 8$ Hz, H-3, 4H), 7.93 (d, $J = 16$ Hz, H-5), 8.02 (s, H-9), 8.03 (s, H-8), 8.11(d, $J = 8$ Hz, H-2, 4H), 8.20 (d, $J = 8.3$ Hz, H-6), 8.26 (d, $J = 16$ Hz, H-4), 8.58 (d, $J = 8.3$ Hz, H-7).

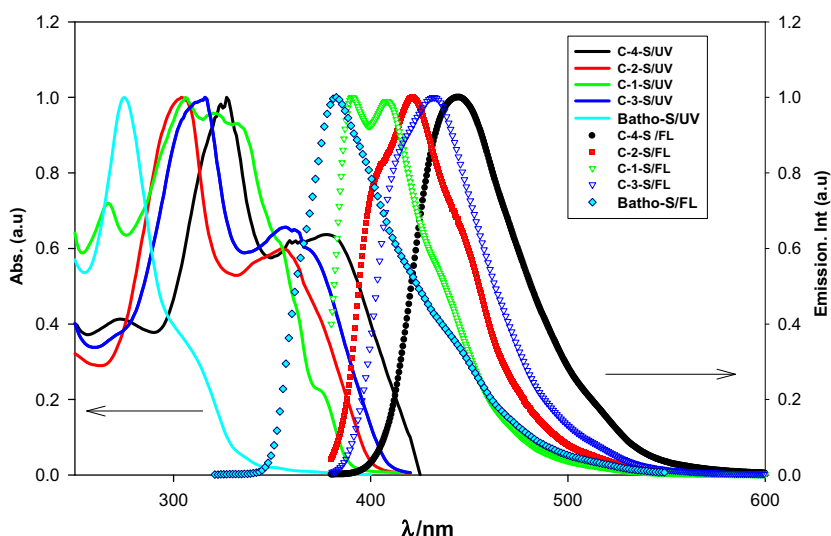
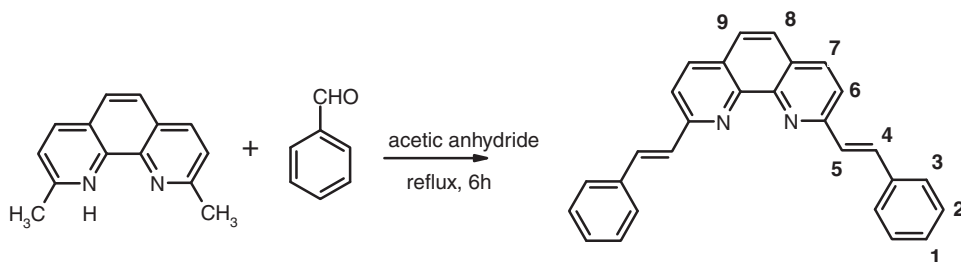
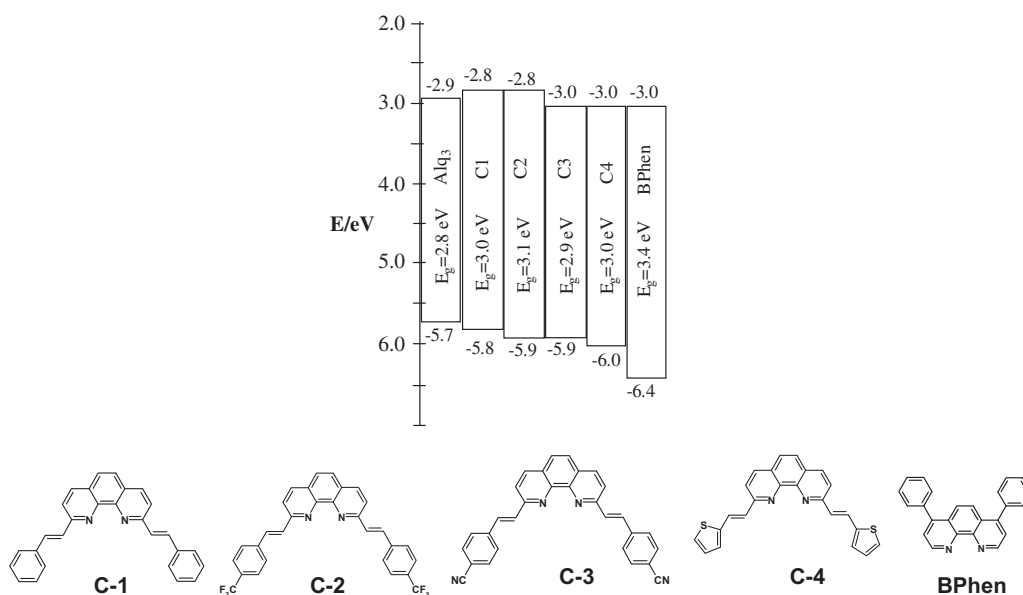


Fig. 2. UV–Vis absorption and fluorescence spectra of C-1 (4.16×10^{-5} M), C-2 (3.84×10^{-5} M), C-3 (5.06×10^{-5} M), C-4 (4.03×10^{-5} M) and BPhen (6.0×10^{-5} M) in CH_2Cl_2 . Excitation wavelengths: C-1, C-2, C-3, C-4 (all 350 nm) except BPhen (300 nm).

Table 1Physical properties of compounds, C-1–C-4 Compared with Alq₃ and bathophen.

Compound	M.p. (°C) (a)	T _g (°C) (a)	T _d (°C) (b)	HOMO (eV) (c)	LUMO (eV) (c)	UV (λ_{max} /nm, absorption) Thin film	FL (λ_{max} /nm, emission) Thin film	Comments
C-1	192	69	300	−5.8	−2.8	277 (m), 340 (sh)	453, 493	Decomposes on sublimation
C-2	279	(d)	337	−5.9	−2.8	279 (m), 345 (sh)	451, 491 (sh)	Stable in OLED production conditions
C-3	289	(d)	130	−5.9	−3.0	313 (m), 362 (sh)	461 (sh), 512	Decomposes on sublimation. So, no device fabricated
C-4	298	111	345	−6.0	−3.0	329(m), 385 (sh)	520	Stable in OLED production conditions
Bathophen (BPhen)	218	62	287	−6.4	−3.0	278 (m), 314 (sh)	385, 402 (sh)	Stable in OLED production conditions. Poor life-time due to low T _g
Alq ₃	415	172	352	−5.7	−2.9	265, 393	520	Stable in OLED production conditions

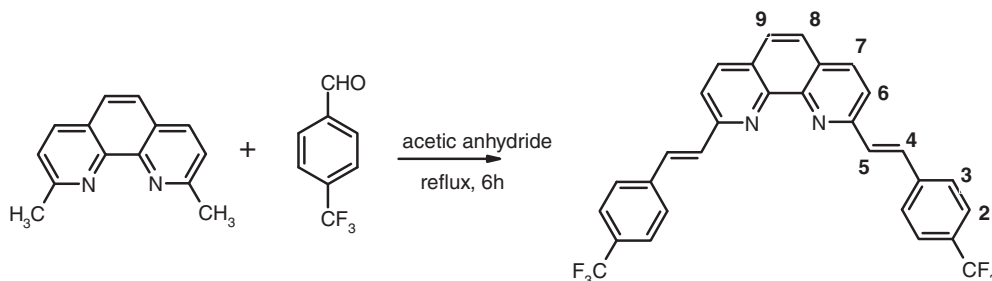
a: Determined by DSC; b: from TGA for 1% mass loss; c: determined from cyclic voltammetry; d: not observed; sh: shoulder.

**Fig. 3.** HOMO–LUMO levels of Alq₃, C-1, C-2, C-3, C-4 and bathophenanthroline (BPhen).

2.1.3. 2, 9-Bis(4,4'-cyanophenyl)vinyl-[1,10]-phenanthroline [C-3]

A mixture of neocuproine hydrate (5.0 g; 0.024 mol) and 4-cyanobenzaldehyde (6.6 g; 0.050 mol) was refluxed in acetic anhydride (30 mL) for 18 h under nitrogen and then allowed to cool to room temperature to give a yellow orange solid. The product was filtered off under suction and washed with petroleum ether (40–60 °C),

methanol and finally with diethyl ether. The product was dried under vacuum at 80 °C to give a light yellow solid (7.9 g; 76%). Finally, the crude product was purified by sublimation (at 280 °C; 10^{−6} Torr) to give an analytically pure material, m.p. 289 °C (DSC, onset). *Anal.* Calc. for C₃₀H₁₈N₄: C, 82.93; H, 4.18; N, 12.82. Found: C, 82.67; H, 4.07; N, 12.82%. The compound was so insoluble in most of the organic solvents that ¹H NMR could not be carried out.



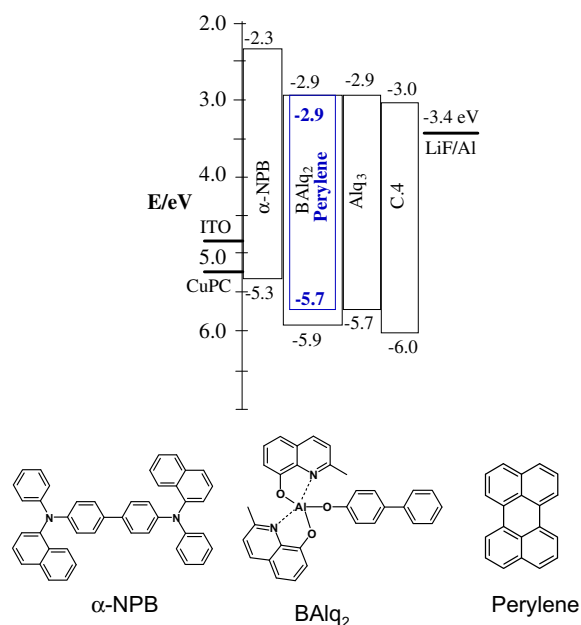


Fig. 4. Energy level diagram for the device: ITO/CuPC(50 nm)/α-NPB (75 nm)/BAQ₂ + perylene(50:0.1 nm)/ETL(20 nm)/LiF(0.5 nm)/Al where the ETL is either Alq₃ or C-4.

2.1.4. 2,9-Bis-(2-thiophen-2-yl-vinyl)-[1,10]phenanthroline [C-4]

A mixture of neocuproine hydrate (50 g; 0.24 mol) and 2-thiophene carboxaldehyde (46.5 mL; 0.50 mol) was refluxed in acetic anhydride (90 mL) for 6 h and then allowed to cool to room temperature over 20 h. Water (20 mL) and methanol (130 mL) were added to the reaction mixture and the product was collected by suction filtration to give a light yellow brown solid. The solid was washed with

petroleum ether (40–60 °C), methanol followed by diethyl ether and dried under vacuum at 80 °C for several hours (>10 h) to give (46 g; 48%) of product. Finally, the product was further purified by sublimation (at 260 °C; 10^{−6} Torr) to give a golden yellow solid, m.p. 298 °C (DSC, onset); *T*_g 111 °C. *Anal.* Calc. for C₂₄H₁₆N₂S₂: C, 72.70; H, 4.07; N, 7.06; S, 16.17. Found: C, 72.85; H, 4.12; N, 7.10; S, 16.17%; ¹H NMR (d-DMF): 7.21(dd, H-2), 7.45 (d, *J* = 16 Hz, H-5), 7.52 (d, *J* = 3.5 Hz, H-3), 7.67 (d, *J* = 5 Hz, H-1), 7.95(s, H-8, 9), 8.15 (d, *J* = 8.3 Hz, H-6), 8.32 (d, *J* = 16 Hz, H-4), 8.49 (d, *J* = 8.3 Hz, H-7). MS (*m/z*) (%): 419 (100) (M⁺+Na), also peaks appeared at *m/z* 435, 472 and 499.

3. Characterisation

UV–Vis absorption spectroscopy (Shimadzu, UV-1601) and fluorescent spectroscopy (Perkin–Elmer LS55) were performed on evaporated thin films on quartz (spectrosil) and in dichloromethane solutions. The decomposition characteristics were examined under nitrogen atmosphere on a TGA equipment (Rheometric Scientific) and the Differential Scanning calorimetry was performed on Perkin Elmer (Pyris 6 DSC). Band gap was estimated from absorption spectroscopy of thin films produced by vacuum thermal evaporation.

HOMO–LUMO levels were determined by cyclic voltammetry (computer controlled potentiostat PAR 273 or CHI 600D, analyte = 0.5 mM, supporting electrolyte (tetrabutyl ammonium tetrafluoroborate = 10 mM in dichloromethane as the solvent). The working, counter and reference electrodes were Pt foil, Pt wire and Ag/AgCl electrodes, respectively.

The HOMO/LUMO levels were determined from the equation in the reference [26]:

$$\text{HOMO/LUMO} = -(E_{1/2} \text{ vs. NHE} + 4.40) \text{ eV} \quad (1)$$

(NHE: normal hydrogen electrode)

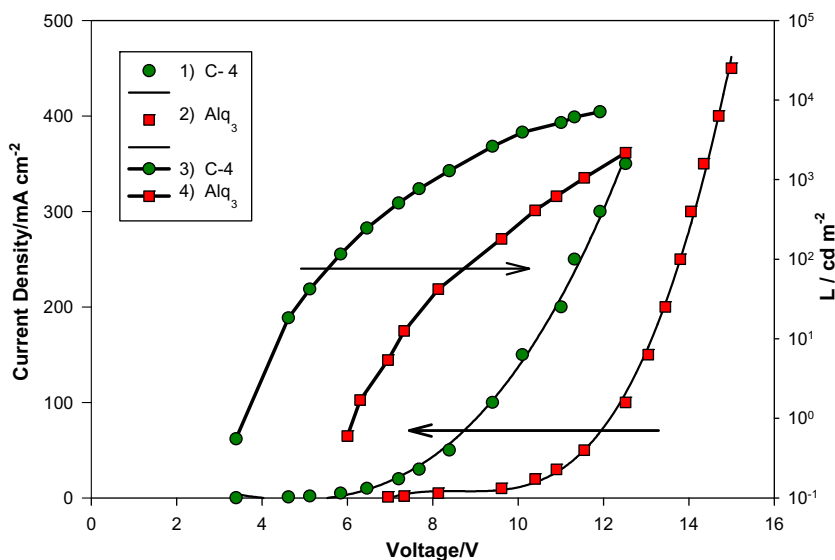
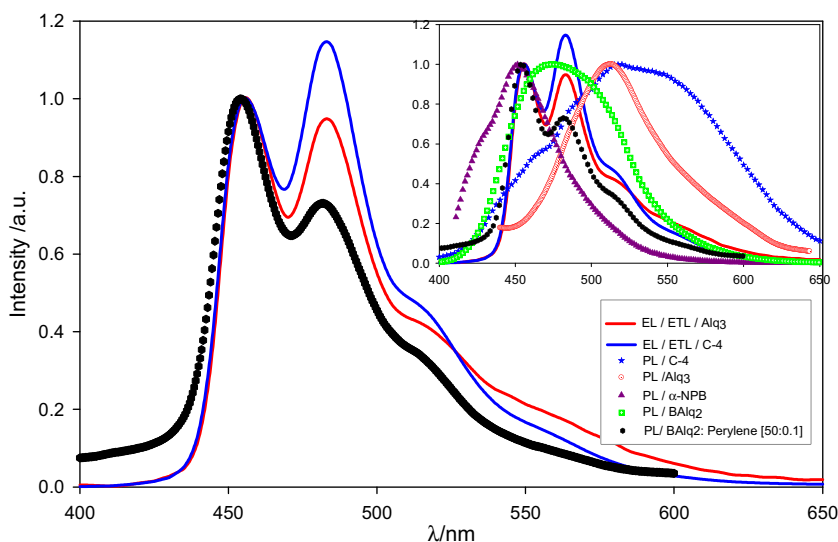


Fig. 5. Current density–voltage–luminance characteristics of ITO/CuPC(50 nm)/α-NPB(75 nm)/BAQ₂ + perylene(50:0.1 nm)/ETL(20 nm)/LiF(0.5 nm)/Al where the ETL is either Alq₃ or C-4.

Table 2

Performance of blue devices (Set A).

ETM	Turn-on voltage (V)	V_{op}/V at 1000 cd m^{-2}	V at 100 mA cm^{-2}	Eff./ cd A^{-1} at 100 cd m^{-2}	Eff./ lm W^{-1} at 100 cd m^{-2}	Eff./ cd A^{-1} at 1000 cd m^{-2}	Eff./ lm W^{-1} at 1000 cd m^{-2}	EQE (%)	Life-time ($t_{1/2}$)/h initial luminance 100 cd m^{-2}
Alq ₃ (a)	6.0	11.0	12.5	1.2	0.5	2.2	0.6	1.54	7200
C-4 (a)	3.5	7.0	8.0	2.3	1.2	2.5	1.1	1.61	3000

(a): ITO/CuPC (50 nm)/ α -NPB (75 nm)/BALq₂ + perylene (50: 0.1 nm)/ETL (20 nm)/LiF (0.5 nm)/Al.**Fig. 6.** EL spectra (solid lines) of ITO/CuPC(50 nm)/ α -NPB(75 nm)/BALq₂ + perylene (50:0.1 nm)/ETL(20 nm)/LiF(0.5 nm)/Al where the ETL is either Alq₃ or C-4. Thin film PL spectra of C-4, Alq₃, α -NPB, BALq₂ and perylene (50:0.1).

The $E_{1/2}$ employed here were determined from the derivative of the cyclic voltammograms.

3.1. Device fabrication

Electroluminescent devices were fabricated by thermal evaporation method using a multi-chamber OLED pilot plant machine (Solciet, manufactured by ULVAC, Japan). The devices were fabricated on a patterned (pixelated) ITO substrate ($40\ \Omega$ per square surface resistance), Hitachi High Tech., Japan), cleaned with deionised water, acetone, isopropyl alcohol and water (in that order), then dried at $150\ ^\circ\text{C}$ for 20 min and then subjected to ozone cleaning (UV irradiation, 185 nm) at $150\ ^\circ\text{C}$ for 10 min. The substrate was then plasma cleaned in the presence of oxygen for 25 s and moved into the vacuum chamber from which the hole injector (copper phthalocyanine, CuPC), hole transporter [N,N' -bis-(1-naphthalenyl)- N,N' -bis-phenyl-(1,1'-biphenyl)-4,4'-diamine (α -NPB)], host (BALq₂ or BH-3):dopant (perylene or BD-3), electron transporter (20 nm) were sequentially deposited under vacuum. The evaporation rates of CuPC, α -NPB, BALq₂, perylene, BH-3, BD-3, Alq₃ and C-4 were 0.7, 1.5, 1, 0.002, 1, 0.1, 1 and $1\ \text{\AA s}^{-1}$, respectively.

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

150 nm). All the devices were encapsulated with a UV curable adhesive (Nagase, Japan) 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. Life time measurements were carried out on encapsulated devices under constant current.

4. Results and discussion

4.1. Physical properties

The thin film absorption and fluorescence spectra of the compounds C-1–C-4 and bathophenanthroline (BPhen) are compared in Fig. 1. The absorbance and fluorescence in dichloromethane are shown in Fig. 2. All the compounds were found to be fluorescent, light blue as thin films and dark blue in solutions.

Table 1 summarises the physical properties of the compounds C-1, C-2, C-3 and C-4. All the compounds were purified by double sublimation.

HOMO–LUMO data are shown in Fig. 3. On substituting the phenyl ring of C-1 with electron withdrawing groups such as CF₃ (C-2), the HOMO level is depressed by 0.1 eV whilst LUMO level is unchanged. In contrast, both HOMO

and LUMO levels are lowered by 0.1 eV on substituting C-1 with the CN group (C-3). This is consistent with the postulation by Bredas and Heeger [20].

4.2. Device performance

As C-1 and C3 decompose on sublimation, they were not suitable for device fabrication under vacuum thermal

evaporation. We report here the blue device performance of only compound 4 as our preliminary results showed that C4 was superior to C2 in terms of operating voltage, efficiency and life-time [22] with green OLEDs. Thus, we fabricated two sets of OLEDs. One (Set A), light blue based on BALq₂ as host and perylene as dopant and the other (Set B) dark blue [(CIE (x, y): (0.15, 0.14))] based on host BH-3 (Kodak) and dopant BD-3 (Kodak).

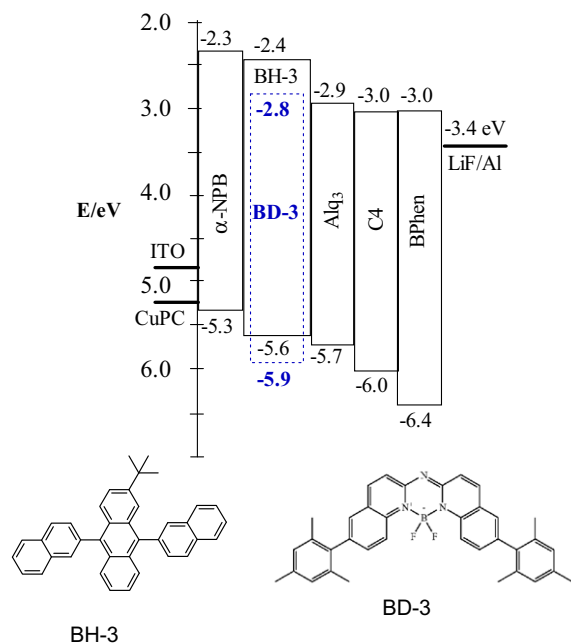


Fig. 7. Energy level diagram for ITO/CuPC (10 nm)/α-NPB(50 nm)/BH-3 + BD-3 (30:0.5 nm)/ETL (20 nm)/LiF(0.5 nm)/Al where the ETL is either Alq₃, C-4 or BPhen.

4.2.1. Device Set A

The device architecture of Set A is ITO/CuPC (50 nm)/α-NPB (75 nm)/BALq₂ + perylene (50:0.1 nm)/ETL (20 nm)/LiF (0.5 nm)/Al where the ETL is either Alq₃ or C-4. The energy level diagram for the device under zero bias is shown in Fig. 4.

Fig. 5 shows the luminance vs. voltage and the current density vs. voltage plots for the Set A. From Fig. 5, it is obvious that the current injection and transport are much more efficient in the case of C-4 as opposed to Alq₃ as evidenced by the lower operating voltage presented by C-4 at any given luminance or current density. For example, the voltage required for devices with Alq₃ as ETM to give a luminance of 1000 cd m⁻² was 11 V as opposed to those with C-4 was only 7 V, a reduction of nearly 36% in operating voltage. Correspondingly, the power efficiency for devices with Alq₃ as ETL was 0.6 lm/W and those with Compound C-4 was 1.1 lm/W at 1000 cd m⁻², representing an increase of 83% in efficiency. The device data are also summarised in Table 2. The colour co-ordinates obtained for devices with Alq₃ [(CIE (x, y): (0.173, 0.252))] and that for the devices with C-4 is (0.150, 0.233). This is consistent with our expectation that the mobility of C-4 is much greater than that of Alq₃ and hence the electron/hole recombination would take place closer to the α-NPB interface for the devices with C-4 and hence more saturated blue colour co-ordinates. Fig. 6 compares the EL spectra of the devices

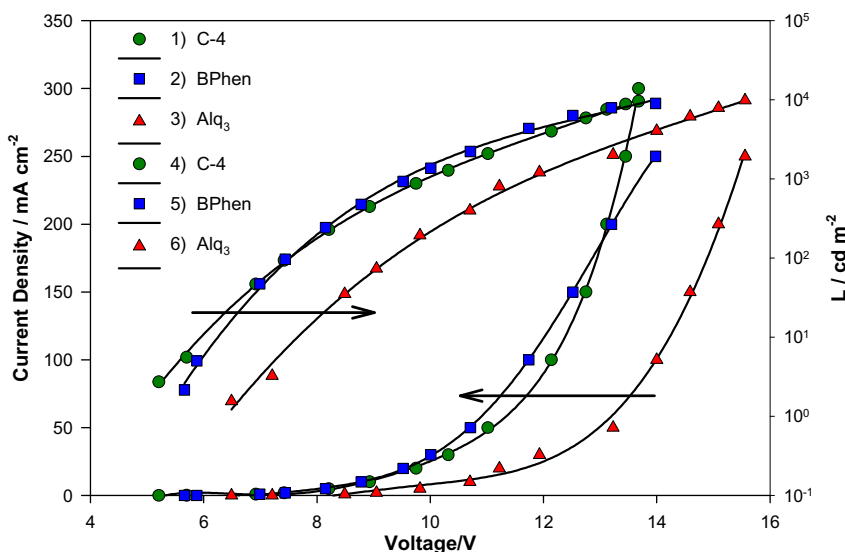


Fig. 8. Current density–voltage–luminance characteristics of ITO/CuPC (10 nm)/α-NPB(50 nm)/BH-3 + BD-3 (30:0.5 nm)/ETL (20 nm)/LiF(0.5 nm)/Al where the ETL is either Alq₃, C-4 or BPhen.

with C-4 and the Alq₃ as ETL and the PL of α -NPB, BAlq₂, a mixture of BAlq₂ with perylene (50:0.1) and Alq₃ and C-4. It is clear from Fig. 6 that the peak positions of the EL spectra and the PL of mixture of BAlq₂ and perylene are identical, but the relative ratios of the intensity of emission are slightly different. The second peak at 483 nm from the EL of the devices with C-4 as the ETL is slightly more intense than the first peak at 455 nm when compared with the EL from devices where Alq₃ is ETL. The EL spectra of devices with Alq₃ has a longer emission tail than the EL spectra of devices with C-4 as the ETL. This explains the differences in colour co-ordinates obtained here. Furthermore, the

relative intensity differences could be due to the slight differences in the concentration of perylene in the host as the control of concentration at such a low level (0.2% of perylene) is not easy under the co-evaporation conditions.

The life-time of the devices with Alq₃ as ETM has significantly longer life-time than C-4. We attribute this to the high T_g (172 °C of Alq₃) as compared to C-4 (111 °C) and the fact that Alq₃ is a mixture of at least two isomers thus retaining a high degree of amorphicity [27].

It is well known that the nature of current injection of an electron transporter is dependent on its interfacial characteristics with the adjacent layer, namely, host + dopant.

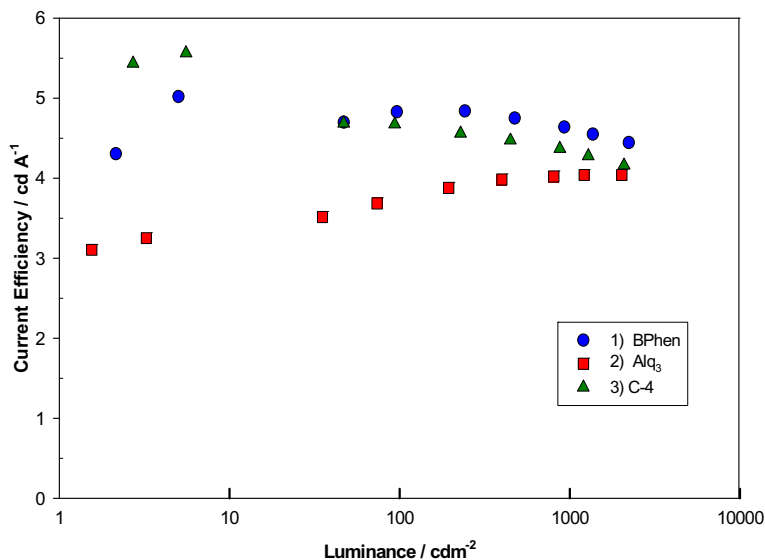


Fig. 9. Current efficiency vs. luminance characteristics of ITO/CuPc (10 nm)/a-NPB (50 nm)/BH-3 + BD-3 (30 + 0.5 nm)/ETL (20 nm)/LiF (0.5 nm)/Al, where the ETL is either Alq₃, C-4 or BPhen.

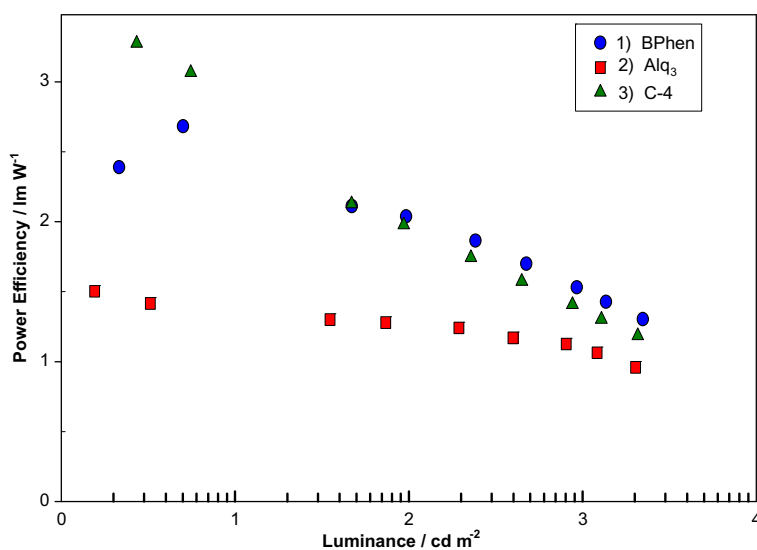


Fig. 10. Power efficiency vs. luminance characteristics of ITO/CuPc (10 nm)/a-NPB (50 nm)/BH-3 + BD-3 (30 + 0.5 nm)/ETL (20 nm)/LiF (0.5 nm)/Al, where the ETL is either Alq₃, C-4 or BPhen.

Table 3
Performance for Blue Devices from Set B.

ETM	Turn-on voltage (V)	V_{op}/V at 1000 cd m^{-2}	V at 100 mA cm^{-2}	Eff./ cd A^{-1} at 100 cd m^{-2}	Eff./ lm W^{-1} at 100 cd m^{-2}	Eff./ cd A^{-1} at 1000 cd m^{-2}	Eff./ lm W^{-1} at 1000 cd m^{-2}	CIE (x, y) at 1000 cd m^{-2}	EQE(%)	Life-time ($t_{1/2}$) at 1000 cd m^{-2}
Alq ₃	6.0 ± 0.2	11.5 ± 0.2	14.0	3.5	1.3	4.0	1.2	(0.152, 0.145)	3.3	1500
BPhen	5.0 ± 0.2	9.5 ± 0.2	12.0	4.5	2.0	4.4	1.4	(0.147, 0.157)	3.4	40
C-4	4.3 ± 0.2	9.5 ± 0.2	12.0	4.6	2.0	4.4	1.6	(0.151, 0.144)	3.6	250

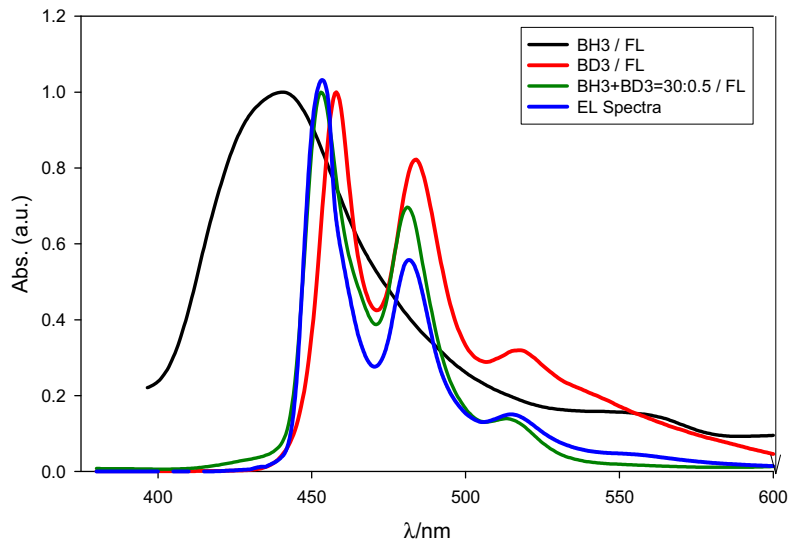


Fig. 11. Fluorescence and EL spectra of ITO/CuPc (10 nm)/ a-NPB (50 nm)/BH-3 + BD-3 (30 + 0.5 nm)/C-4 (20 nm)/LiF (0.5 nm)/Al.

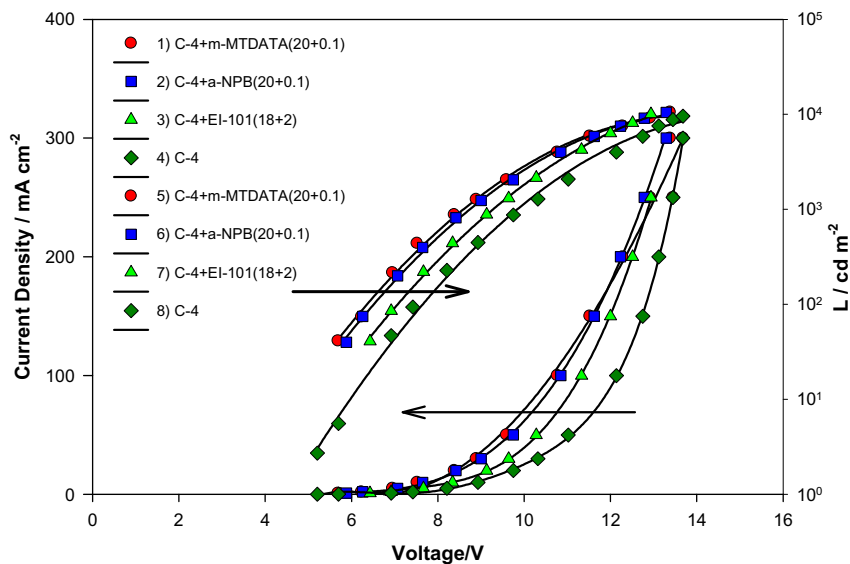


Fig. 12. Current density vs. voltage vs. luminance for ITO/CuPc (10 nm)/a-NPB (50 nm)/BH-3 + BD-3 (30 + 0.5 nm)/C-4 (20 nm)/LiF (0.5 nm)/Al where C-4 was doped with m-MTDATA (0.5%), a-NPB (0.5 %) and Liq (10%).

The question is whether C-4 would perform well in another system. Further, the comparison of the electron transporter, C-4 with Alq₃ alone is not sufficient as it is known that bathophenanthroline (BPhen) has much higher electron mobility and deeper HOMO level than Alq₃, any new ETM has to be compared with BPhen as well. Thus, we designed the device structure Set B to compare C-4 with BPhen and Alq₃.

4.2.2. Device Set B

ITO/CuPc (10 nm)/ α -NPB (50 nm)/BH-3 + BD-3 (30:0.5 nm)/ETL (20 nm)/LiF (0.5 nm)/Al where the ETL is either Alq₃, C-4 or BPhen. The energy level diagram for the devices in Set B is shown in Fig. 7.

Figs. 8–10 show the luminance vs. voltage, current density vs. voltage, current efficiency (cd/A) vs. luminance and power efficiency (lm/W) vs. luminance for Set B. Reduction in operating voltage with C-4 is again substantial. The turn-on voltage for the devices with C-4, BPhen and Alq₃ are 4.3, 5.0 and 6.0 V, respectively (Table 3). A 17% reduction in operating voltage and 33% increase in power efficiency has been achieved by replacing Alq₃ with C-4 at 1000 cd m⁻². The current injection from C-4 is similar to that of BPhen.

We attribute the low turn-on voltage and operating voltage of C-4 to its high mobility. The EL and PL spectra of BH-3, BD-3 and a mixture of BH-3 and BD-3 (30:0.5) are shown in Fig. 11. The PL spectra of the mixture is blue shifted by 4 nm compared to virgin BD-3 as expected. The EL spectra of the devices in Set B are identical to the PL of the mixture. Thus, the same excited state is involved in both the cases.

It has to be stressed that interfacial effects dominate OLED performance and the electron transporter/host + dopant interface is no exception. Thus, a good electron transporter for one particular system may not be as good in another system even if the mobilities of the ETM's are high. What is required is a balanced injection of electrons and holes.

The life time at 1000 cd m⁻² for C-4 is 6.25 times longer than that for BPhen as ETL. We attribute the enhanced life-time from devices with C-4 to its higher T_g of 111 °C as opposed to the lower T_g of 62 °C for BPhen.

Though, the life-time of devices with C-4 is longer than that with BPhen, they are not as long as Alq₃. It is general practice to dope the electron transporters with lithium quinolinolate (Liq) to improve the life time of devices

[23]. Okumoto and Kanno reported that doping of the electron transporters with hole transporters such as m-MTDATA, α -NPB resulted in reduction in operating voltage and increased life-time [18]. We fabricated devices of the Type C (ITO/CuPc (10 nm)/ α -NPB (50 nm)/BH-3 + BD-3 (30:0.5 nm)/C-4 (20 nm)/LiF (0.5 nm)/Al) where the compound 4 is doped with m-MTDATA (0.5%), α -NPB (0.5%) and Liq (10%) and found that the turn-on voltage and the operating voltages are indeed reduced (Fig. 12). The performances of the devices are summarised in Table 4.

We found that m-MTDATA as the dopant was most effective in reducing the operating voltage, then α -NPB and Liq. However, there was no significant gain in either the current efficiency or power efficiency.

Fig. 13 shows the energy level diagram for device Type C. The turn-on voltage of the doped systems simply follow the energy difference between LUMO level of the dopants and LUMO level of the host ETM (C-4). The difference of energy between the LUMO levels of the dopants, m-MTDATA, α -NPB and Liq and C-4 are 1.1, 0.7 and 0.5 eV which correlate with the turn on-voltage of 3.8, 4.1 and 4.2 V, respectively. The diminution of the turn on voltage and operating voltage could be attributed to charge transfer from the donor molecules to the acceptor (C-4), thereby increasing the conductivity [24,25]. Life-time measurements of the doped systems are on going and will be reported elsewhere.

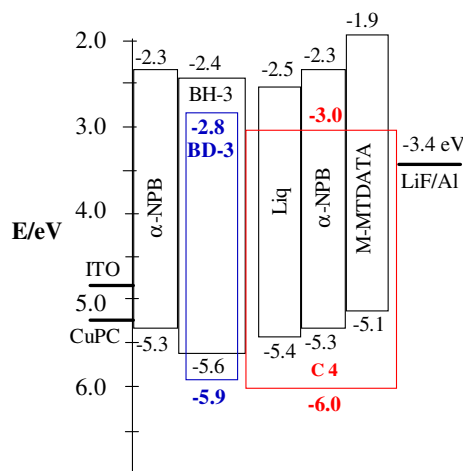


Fig. 13. Energy level diagram for ITO/CuPc (10 nm)/ α -NPB (50 nm)/BH-3 + BD-3 (30 + 0.5 nm)/C-4 (20 nm)/LiF (0.5 nm)/Al where C-4 was doped with m-MTDATA (0.5%), α -NPB (0.5%) and Liq (10%).

Table 4

Device Performance of C-4 with m-MTDATA, α -NPB and Liq as dopants.

ETM	Turn-on voltage (V)	V_{op}/V at 1000 cd m ⁻²	V at 100 mA cm ⁻²	Eff./cd A ⁻¹ at 100 cd m ⁻²	Eff./lm W ⁻¹ at 100 cd m ⁻²	Eff./cd A ⁻¹ at 1000 cd m ⁻²	Eff./lm W ⁻¹ at 1000 cd m ⁻²	EQE (%)	CIE (x, y) at 1000 cd m ⁻²
Compound 4 (C-4)	4.3	9.5	12.0	4.6	2.0	4.4	1.6	3.6	(0.151, 0.144)
C-4 + m-MTDATA (0.5%)	3.8	8.7	10.5	4.8	2.4	4.6	1.7	3.6	(0.152, 0.155)
C-4 + α -NPB (0.5%)	4.1	8.7	10.5	4.0	2.2	4.2	1.6	3.5	(0.146, 0.139)
C-4 + Liq (10%)	4.2	9.0	11.5	4.3	1.8	4.4	1.6	3.6	(0.148, 0.143)

5. Conclusion

We have demonstrated that it is possible to produce phenanthroline derivatives for example, 2,9-bis-(2-thiophen-2-yl-vinyl)-[1,10]phenanthroline (C-4) which can act as good electron transporters and hole blockers with reasonably long life-times even in their virgin form. Further synthetic work is in progress to identify phenanthroline derivatives which would give much longer life-time than Alq₃ or doped BPhen.

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