Supporting information

Bifunctioned Anthracene Derivatives as Non Doped Blue Emitters and Hole-Transporters for Electroluminescent Devices

A. Thangthong, D. Meunmart, N. Prachumrak, S. Jungsuttiwong, T. Keawin, T. Sudyoadsuk and V. Promarak*

Center for Organic Electronic and Alternative Energy, Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Ubon Ratchathani University, Warinchumrap, Ubon Ratchathani, 34190 (Thailand)

Fax: (+66) 45 288379 E-mail: pvinich@ubu.ac.th; pvinich@gmail.com

General Procedure

All reagents were purchased from Aldrich, Acros or Fluka and used without further purification. All solvents were supplied by Thai companies and used without further distillation.Tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and distilled. Dichloromethane for cyclic voltammetry (CV) measurements was washed with conc. H_2SO_4 and distilled twice from calcium hydride.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Brüker AVANCE 300 MHz spectrometer with tetramethylsilane as the internal reference using $CDCl_3$ as solvent in all cases. Infrared (IR) spectra were measured on a Perkin-Elmer FTIR spectroscopy spectrum RXI spectrometer as potassium bromide (KBr) disc. Ultraviolet-visible (UV-Vis) spectra were recorded as a diluted solution in spectroscopic grade dichloromethane on a Perkin-Elmer UV Lambda 25 spectrometer. Photoluminescence spectra and the fluorescence quantum yields (Φ_F) were recorded with a Perkin-Elmer LS 50B Luminescence Spectrometer as a dilute solution in spectroscopic grade dichloromethane and thin film obtained by thermal deposition.

The fluorescence quantum yields (Φ or Φ_F) were determined by comparison with a fluorescence standard of known fluorescence quantum yield value according to the following equation:[1]

$$\Phi_X = \Phi_{ST}\left(\frac{Slope_X}{Slope_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right)$$

Where the subscripts X refer to the unknown samples and ST refers to the standard quinine sulfate solution in 0.01 M H_2SO_4, whose fluorescence quantum yield is known to be 0.54. $\Phi$is the fluorescence quantum yield, Slope is the slope from the plot of integrated fluorescence intensity vs absorbance, and η is the refractive index of the solvent. The refractive indexes of the solvents were taken as 1.424 and 1.333 for CH_2Cl_2 and 0.01 M H_2SO_4, respectively (for the detail see the supporting information).

Differential scanning carolimetry (DSC) analysis and thermogravimetry analysis (TGA) were performed on a METTLER DSC823e thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer, respectively, with heating rate of 10 ^{o}C/min under nitrogen atmosphere. Cyclic voltammetry (CV) measurements were carried out on an Autolabpotentiostat PGSTAT 12 with a three electrode system (platinum counter electrode, glassy carbon working electrode and Ag/Ag^+ reference electrode) at scan rate of 50 mV/s in dichloromethane under argon atmosphere. The concentration of analytical materials and tetrabutyl ammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) were 10^{-3} Mand 0.1 M, respectively.

Materials synthesis and characterizations

Scheme 1. Synthetic route of **1** and **2**: i) Pd(PPh$_3$)$_4$, 2M Na$_2$CO$_3$, THF.

Synthesis of 9-bromo-10-(9,9-di-*n*-hexylfluoren-2-yl)anthracene (4)

A mixture of 2-iodo-9,9-bis-*n*-hexylfluorene (1.28 g, 2.79 mmol), 9-bromoanthracen-10-boronic acid (0.84 g, 2.79 mmol) and Pd(PPh$_3$)$_4$(0.065 g, 0.12 mmol) and 2 M Na$_2$CO$_3$ (8 ml,) aqueous solution in THF (12 ml) was degassed with N$_2$ for 5 min. The reaction mixture was stirred at reflux under N$_2$ for 18 h. After being cooled to room temperature, water (50 ml) was added and extracted with CH$_2$Cl$_2$ (50 ml x 2). The combined organic phase was washed with water (50 ml), brine solution (50 ml), dried over anhydrous Na$_2$SO$_4$, filtered, the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH$_2$Cl$_2$ and hexane (1:4) followed by recrystallization from a mixture of CH$_2$Cl$_2$ and methanol afforded light yellow solid (0.66 g, 52%); ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.76-0.88 (10 H, m), 1.09-1.14 (12 H, m), 1.95-2.01 (4H, m), 7.34-7.40 (7 H, m), 7.59 (2 H, t, *J* = 8.8 Hz), 7.72 (2 H, d, *J* = 9.0 Hz), 7.81 (1 H, dd, *J* = 3.3 Hz, J = 2.7 Hz), 7.89 (1 H, d, *J* = 7.5 Hz) and 8.62 (2 H, d, *J* = 8.7 Hz); ^{13}C-NMR (75Hz, CDCl$_3$) δ 13.99, 22.47, 23.85, 29.60, 31.52, 40.37, 55.26, 119.62, 119.83, 122.92, 124.87, 125.46, 125.91, 126.54, 126.92, 127.32, 127.44, 129.73, 130.30, 131.20, 136.90, 140.81 and 150.95; HRMS-ESI m/z: [MH$^+$] calcd. for C$_{39}$H$_{42}$Br, 589.2432; found, 589.3042.

Synthesis of 9-((9,9-di-*n*-hexylfluoren-2-yl)-10-(*N*,*N*-diphenyl-*N*-4-aminophenyl) anthracene (1)

A mixture of **4** (0.52 g, 0.88 mmol), *N*,*N*-diphenyl-*N*-4-aminophenylboronic acid(0.28 g, 0.97 mmol), Pd(PPh$_3$)$_4$ (0.021 g, 0.017 mmol) and 2 M Na$_2$CO$_3$ aqueous solution (6 ml) in THF (10 ml) was degassed with N$_2$ for 5 min. The reaction mixture was stirred at reflux under N$_2$. After being cooled to room temperature, water (50 ml) was added and extracted with CH$_2$Cl$_2$ (50 ml x 2). The combined organic

phase was washed with water (50 ml), brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:4) followed by recrystallization from a mixture of CH_2Cl_2 and methanol afforded light yellow solids (0.52 g, 79%); ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.75-0.80 (10 H, m), 1.09-1.16 (12 H, m), 1.98-2.03 (4 H, m), 7.07-7.12 (2 H, t, J = 7.0 Hz), 7.26-7.46 (21 H, m), 7.77-7.95 (6 H, m); ^{13}C-NMR ([75] MHz, CDCl$_3$) δ 14.02, 22.51, 23.89, 31.55, 40.47, 55.26, 119.61, 119.78, 122.91, 123.10, 123.13, 124.71, 124.97, 126.16, 126.88, 127.10, 127.19, 129.40, 129.89, 130.10, 130.15, 132.14, 132.69, 136.92, 137.70, 140.54, 141.00, 147.17, 147.84, 150.86 and 150.98; IR (KBr) 2929, 1590, 1494, 1380, 1273, 1019, 823 and 746 cm^{-1}; HRMS-ESI m/z: [MH$^+$] calcd. for $C_{57}H_{56}N$, 754.4407; found, 754.4386.

Synthesis of 2,7-bis-(9-bromoanthracen-10-yl)-9,9-(di-*n*-hexyl)fluorene (6)

A mixture of 2,7-diiodo-9,9-bis-*n*-hexylfluorene (1.11 g, 1.90 mmol), 9-bromoanthracen-10-boronic acid (1.20 g, 3.99 mmol) and Pd(PPh$_3$)$_4$(0.11 g, 0.10 mmol) and 2 M Na_2CO_3 (10 ml,) aqueous solution in THF (15 ml) was degassed with N_2 for 5 min. The reaction mixture was stirred at reflux under N_2 for 20 h. After being cooled to room temperature, water (50 ml) was added and extracted with CH_2Cl_2 (50 ml x 2). The combined organic phase was washed with water (50 ml), brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:4) followed by recrystallization from a mixture of CH_2Cl_2 and methanol afforded light yellow solid (0.90 g, 56%); ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.8 (6 H, t, J = 6.9 Hz), 0.94 (4 H, m), 1.14-1.27 (12 H, m), 2.04 (4 H, t, J = 7.8 Hz), 7.40-7.48 (8 H, m), 7.65 (4 H, t, J = 8.4 Hz), 7.79 (4 H, d, J = 9.0 Hz), 8.04 (2 H, d, J = 8.1 Hz) and 8.66 (4 H, d, J = 9.0 Hz); ^{13}C-NMR (75Hz, CDCl$_3$) δ 14.02, 22.40, 24.06, 29.55, 31.57, 40.34, 55.51, 119.86, 122.70, 125.56, 126.04, 126.97, 127.40, 127.95, 130.01, 130.34, 131.21, 137.32, 138.229, 140.53 and 151.21; HRMS-ESI m/z: [MH$^+$] calcd. for $C_{53}H_{49}Br_2$, 843.2193; found, 843.8920.

Synthesis of 2,7-bis-(9-(*N,N*-diphenyl-*N*-4-aminophenyl)anthracen-10-yl)-9,9-(di-*n*-hexyl)fluorene (2)

A mixture of **6** (0.51 g, 0.60 mmol), *N,N*-diphenyl-*N*-4-aminophenylboronic acid(0.37 g, 1.27 mmol), Pd(PPh$_3$)$_4$ (0.01 g, 0.01 mmol) and 2 M Na_2CO_3 aqueous solution (6 ml) in THF (10 ml) was degassed with N_2 for 5 min. The reaction mixture was stirred at reflux under N_2. After being cooled to room temperature, water (50 ml) was added and extracted with CH_2Cl_2 (50 ml x 2). The combined organic phase was washed with water (50 ml), brine solution (50 ml), dried over anhydrous Na_2SO_4, filtered, the solvents were removed to dryness. Purification by column chromatography over silica gel eluting with a mixture of CH_2Cl_2 and hexane (1:6) followed by recrystallization from a mixture of CH_2Cl_2 and methanol affordeddeep yellow solids (0.45 g, 75%); ^{1}H-NMR (300 MHz, CDCl$_3$) δ 0.82 (6 H, t, J = 6.9 Hz), 0.91 (4 H, bs), 1.17-1.28 (12 H, m), 2.06 (4 H, t, J = 7.8 Hz), 7.12 (4 H, t, J = 6.9 Hz), 7.31-7.48 (32 H, m), 7.55-7.56 (4 H, m), 7.85 (4 H, d, J = 8.7 Hz), 7.90 (4 H, d, J = 8.4 Hz) and 8.07 (2 H, d, J = 8.1 Hz); ^{13}C-NMR (75 MHz, CDCl$_3$) δ 14.05, 22.48, 24.10, 29.65, 31.62, 40.51, 55.50, 119.77, 123.12, 124.73, 125.02, 126.28, 127.07, 127.16, 129.41, 130.14, 130.20, 132.16, 132.70, 137.00, 137.55, 137.96, 140.43, 147.20, 147.85 and 151.18; IR (KBr) 2922, 1590, 1491, 1384, 1273, 1019, 823 and 764 cm^{-1}; HRMS-ESI m/z: [MH$^+$] calcd. for $C_{89}H_{77}N_2$, 1173.6081; found, 1173.6070.
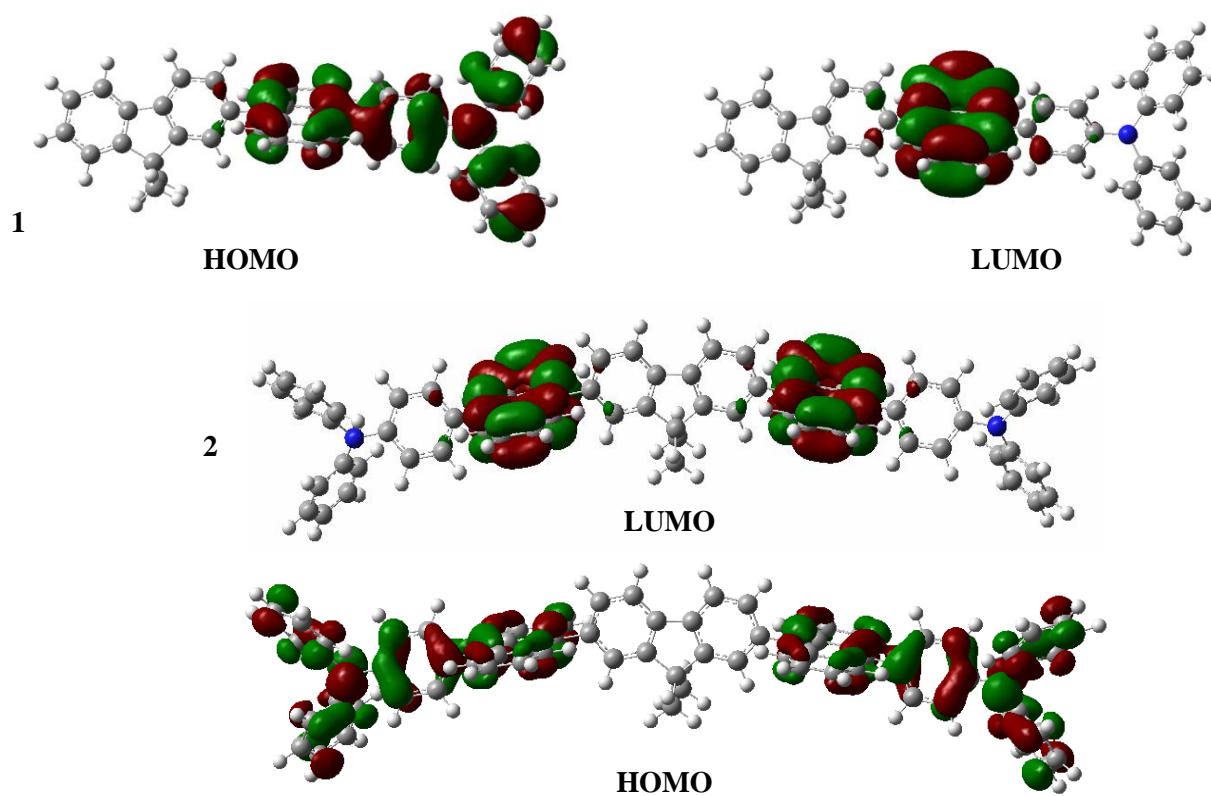
Computer quantum calculation results

The ground state geometries of **1** and **2** were fully optimized using density functional theory (DFT) at the B3LYP/6-31G (d,p) level, as implemented in Gaussian 03.36 TDDFT/B3LYP calculation of lowest excitation energies were performed at the optimized geometries of the ground states.[2]
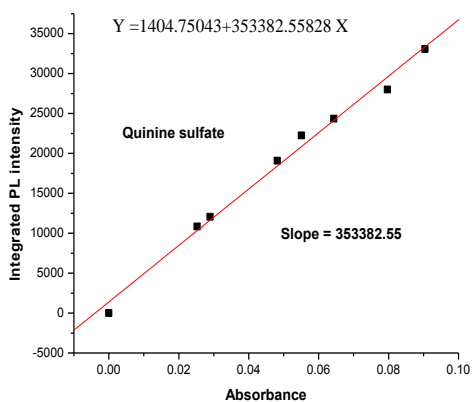
Optimized geometries of 1 and 2

1

2
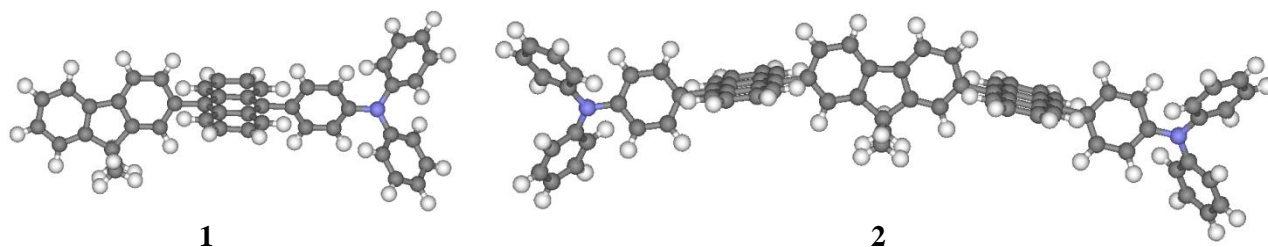
Figure 1. The optimized geometries of **1** and **2**

HOMO-LUMO orbitals of 1 and 2

1

HOMO

LUMO

2

LUMO

HOMO

Figure 2. The HOMO and LUMO orbitals of **1** and **2**

2. Fluorescence quantum yields (Φ) measurement

Y =1404.75043+353382.55828 X

Quinine sulfate

Slope = 353382.55

S4
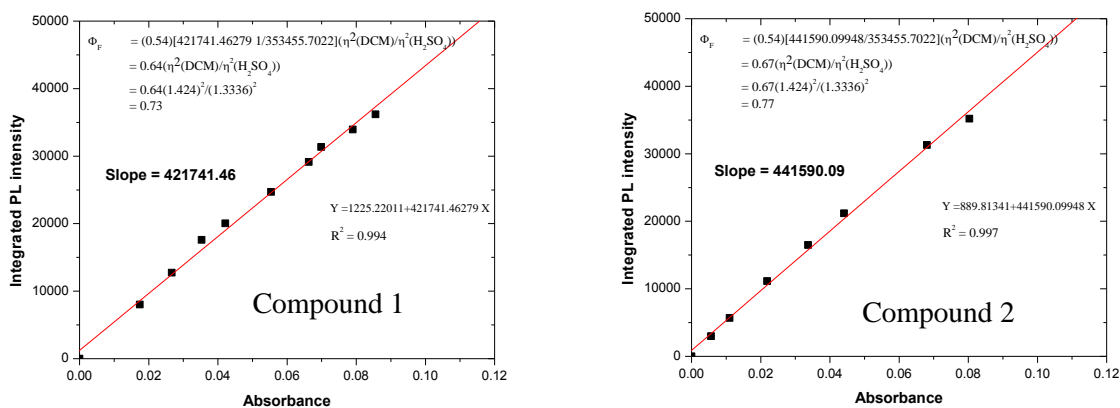
Figure 3. Plots of integrated fluorescence intensity *vs* absorbance and calculation

3. UV-Vis and PL spectra, CV and multiple CV scans, DSC and TGA thermograms of compounds 1 and 2
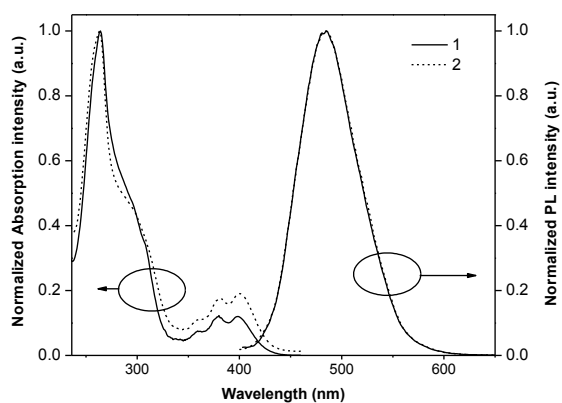

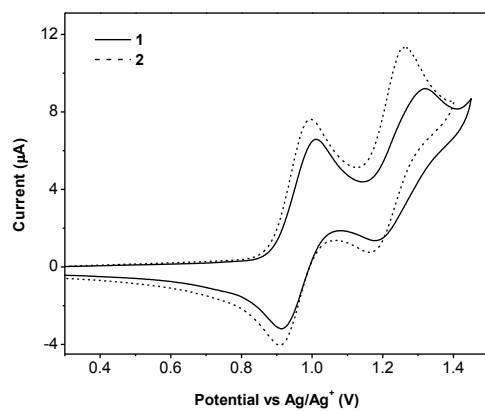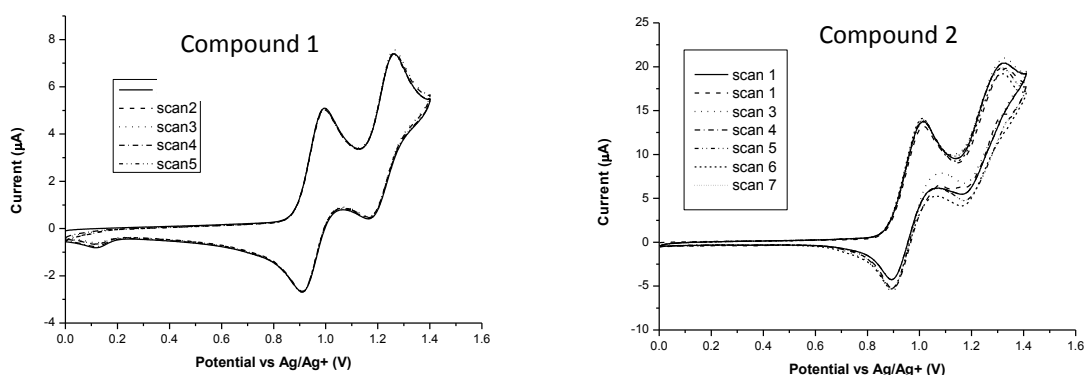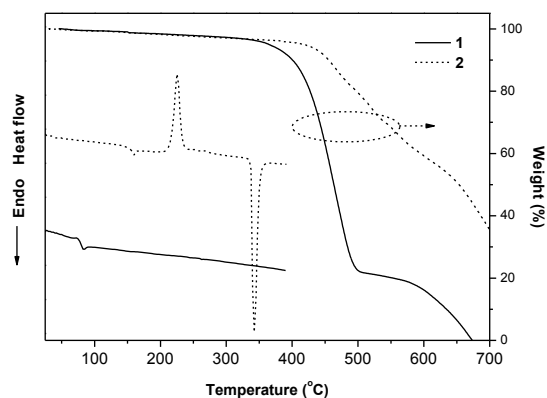**Figure 4.** UV-vis absorption and PL spectra of **1** and **2** measured in dilute CH_2Cl_2 solution

Figure 5. CV curves of **1** and **2** measured in CH_2Cl_2 at a scan rate of 50 mV/s.

**Figure 6.** Multile CV curves of **1** and **2** measured in CH_2Cl_2 at a scan rate of 50 mV/s.

Figure 7. DSC (2nd heating scan) and TGA thermograms of **1** and **2** measured under N_2 at heating rate of 10 °C/min

Fabrication and Characterisation of OLEDs.

   OLED devices using **1** and **2** as EL with configuration of ITO/PEDOT:PSS/EL(50 nm)/BCP(40 nm)/LiF(0.5 nm):Al(150 nm) and double-layer green OLED devices using **1**, **2** and NPB as HTL with configuration ITO/PEDOT:PSS/HTL(40 nm)/Alq3(50 nm)/LiF(0.5 nm):Al(150 nm) were fabricated and characterized as followed. The patterned indium tin oxide (ITO) glass substrate with a sheet resistance 14 $\Omega/\square$ (purchased from Kintec Company) was thoroughly cleaned by successive ultrasonic treatment in detergent, deionised water, isopropanol, and acetone, and then dried at 60 °C in a vacuum oven. A 50 nm thick PEDOT:PSS hole injection layer was spin-coated on top of ITO from a 0.75 wt.% dispersion in water at a spin speed of 3000 rpm for 20 s and dried at 200 °C for 15 min under vacuum. Thin films of each organic EL or HTL were deposited on top of PEDOT:PSS layer by evaporation from resistively heated alumina crucibles at evaporation rate of 0.5-1.0 nm/s in vacuum evaporator deposition (ES280, ANS Technology) under a base pressure of $\sim 10^{-5}$ mbar. The film thickness was monitored and recorded by quartz oscillator thickness meter (TM-350, MAXTEK). A 40 nm thick hole-blocking layer of BCP or a 50 nm thick green-emitting layer of Alq3 was then deposited on the organic EL or HTL, respectively, without breaking the vacuum chamber. The chamber was vented with dry air to load the cathode materials and pumped back; a 0.5 nm thick LiF and a 150 nm thick aluminium layers were the subsequently deposited through a shadow mask on the top of EL/HTL film without braking vacuum to from an active diode areas of 4 mm^2. The measurement of device efficiency was performed according to M.E.

Thomson's protocol and the device external quantum efficiencies were calculated using procedure reported previously.[3] Current density-voltage-luminescence (*J-V-L*) characteristics were measured simultaneous by the use of a Keithley 2400 source meter and a Newport 1835C power meter equipped with a Newport 818-UV/CM calibrated silicon photodiode. The EL spectra were acquired by an Ocean Optics USB4000 multichannel spectrometer. All the measurements were performed under ambient atmosphere at room temperature.
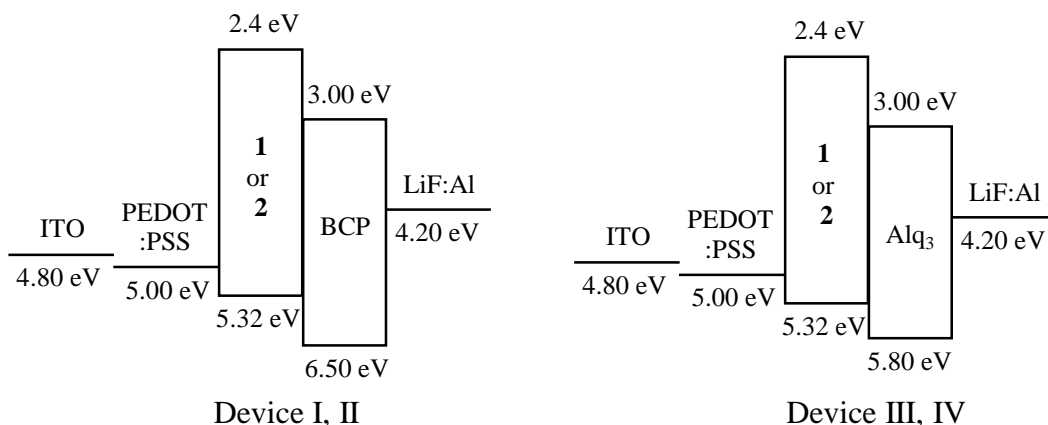
Figure 8. Band energy diagram of OLED devices with **1** and **2** as EL and HTL
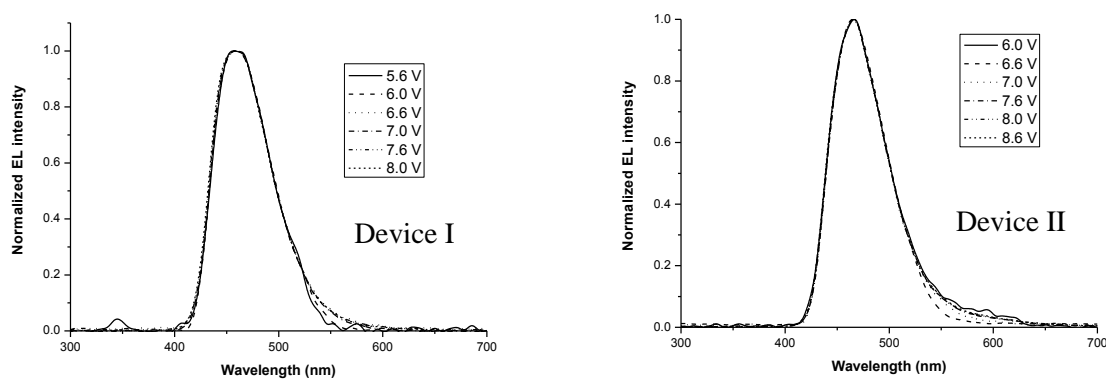
Figure 9. Normalized EL spectra of OLED devices I and II under differnent applied voltages.
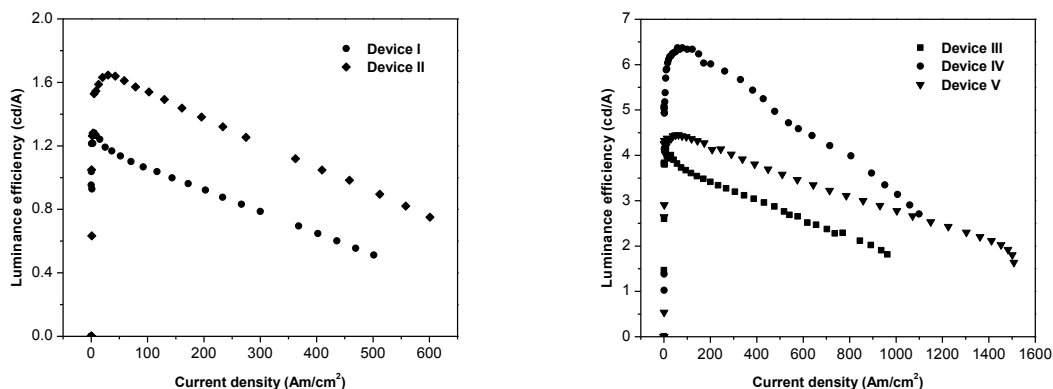
Figure 10. Variation in luminance efficiency with current density of OLED devices.

References

1   T. Kartens, K. Kobs, *J. Phys. Chem.*, 1980, **84**, 1871-1872.

2   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A., Jr. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 98, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

3   S. R. Forrest, D. D. C. Bradley, M. E. Thomson, *Adv. Mater.*, 2003, **15**, 1043-1048.