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Synthesis and Electroluminescent Properties of Blue Fluorescent Triphenylamine Substituted Anthracene Derivatives for OLEDs

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*We describe the electroluminescent properties of blue fluorescent materials based on mono(triphenylamino)anthracene derivatives synthesized via Suzuki cross coupling reactions. To explore the electroluminescent properties of materials **1–3**, multi-layered OLEDs were fabricated and all devices exhibited efficient blue emissions. Among those, device **1**, with CIE x,y coordinates of (0.159, 0.166) at 12.0 V, exhibited the best performance, with a maximum luminance of 7306 cd/m² at 12.0 V, and luminous and power efficiencies of 4.95 cd/A and 1.83 lm/W at 20 mA/cm², respectively.*

Introduction

The development of highly efficient organic light-emitting diodes (OLEDs) has attracted significant attention recently due to its potential application in flat panel displays [1–4]. In this regards a variety of new emitting materials have been developed to fill the requirements of three primary color (red, green, blue) emitters for full color OLED displays [5]. However, blue-emitting materials still receive considerable attention, because its wide band gap is such that highly efficient deep blue emitting materials are difficult to produce. Recently, a variety of blue-emitting materials based on anthracene have been reported [6–16]. Among these are mono(triarylamino)-substituted anthracene derivatives. For example, Tao et al. have reported that 9-mono(triphenylamino)-10-pyrenyl anthracene derivatives exhibited efficient blue emission with a maximum efficiency of up to 7.9 cd/A in a nondoped

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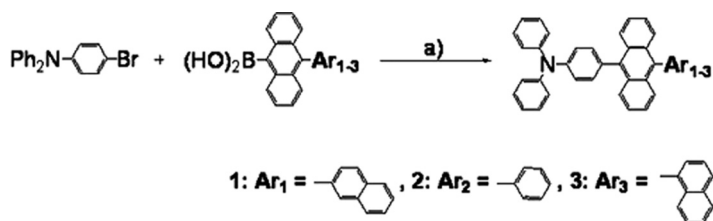
Figure 1. Synthetic routes to blue fluorescent materials (**1–3**). Conditions: a) Pd(PPh$_3$)$_4$, K$_2$CO$_3$ (2 M in H$_2$O), Aliquat 336, Toluene, reflux.

device [17]. However, for practical applications, the properties of these emitting materials need to be improved.

In this study, a series of blue fluorescent materials (**1–3**) based on mono(triphenylamino) anthracene (Figure 1) were synthesized, and their electroluminescent properties were investigated in doping system using ADN as a host [7].

Experimental

Materials and Characterization

9-(naphthalen-2-yl)-10-(4-triphenylamine)anthracene (**1**) and 9-phenyl-10-(4-triphenylamine) anthracene (**2**) were prepared according to literature methods [18]. ^{1}H- and ^{13}C-NMR were recorded using a Varian (Unity Inova 300NB) or Varian (Unity Inova 500NB) spectrometer at 300 MHz and 500 MHz, respectively. Low- and high-resolution mass spectra were recorded using a Jeol JMS-AX505WA spectrometer in FAB mode or Jeol JMS-600 spectrometer in EI mode.

9-(naphthalen-1-yl)-10-(4-triphenylamine)anthracene (**3**). A solution of 4-bromo-*N,N*-diphenylaniline (0.64 mmol), 10-phenylanthracen-9-ylboronic acid (0.84 mmol), tetrakis(triphenyl phosphine)palladium (0.02 mmol), Aliquat 336 (0.05 mmol) and aqueous 2.0 M K$_2$CO$_3$ (5.20 mmol) in toluene were heated at 120°C under Ar atmosphere for 4 h. After the solution cooled, the product was extracted with CH$_2$Cl$_2$. The CH$_2$Cl$_2$ solution was washed with brine and H$_2$O, and then dried on MgSO$_4$. Evaporation of the solvent, followed by recrystallization with CHCl$_3$/hexane, gave **3** (92%) as a yellow solid. ^{1}H-NMR (300 MHz, CDCl$_3$): δ ppm 8.06 (d, $J = 8.2$ Hz, 1H), 8.01 (d, $J = 8.2$ Hz, 1H), 7.89 (d, $J = 8.8$ Hz, 2H), 7.70 (t, $J = 7.0$ Hz, 1H), 7.56 (d, $J = 7.0$ Hz, 1H), 7.51–7.15 (m, 21H), 7.12–7.06 (m, 2H); ^{13}C-NMR (500 MHz, CDCl$_3$): ppm 148.0, 147.4, 137.6, 137.1, 135.0, 133.9, 133.8, 132.8, 132.4, 130.9, 130.3, 129.6, 129.4, 128.4, 128.3, 127.3, 127.2, 126.9, 126.5, 126.2, 125.8, 125.4, 125.2, 124.9, 123.4, 123.3, 123.2; IR (KBr): ν 3037, 1592, 1509, 1493, 1374, 1326, 1279, 936, 762, 755, 738, 697 cm^{-1}; EI-MS $m/z = 547$ [M$^+$]; HRMS-TOF [M$^+$ + H] Anal. calcd for C$_{50}$H$_{53}$N$_2$ 547.2300: found 547.2273.

Physical Measurements

The UV-Vis absorption and photoluminescence spectra of these newly designed dopants were measured in CH$_2$Cl$_2$ solution (10^{-5} M) using a Sinco S-3100 and Amincobrowman series 2 luminescence spectrometer, respectively. The HOMO energy levels were determined by low energy photoelectron spectrometry

(Riken-Keiki AC-2). LUMO energy levels were estimated by subtracting the energy gap from the HOMO energy levels.

OLED Fabrication and Measurement

For fabricating the OLEDs, indium-tin-oxide (ITO) thin films coated on glass substrates were used, with a sheet resistivity of $30\,\Omega$/square and a thickness of $100\,nm$. The ITO-coated glass was cleaned in an ultrasonic bath by the following sequence of solvents: acetone, methyl alcohol, and distilled water, and kept in isopropyl alcohol for $48\,h$ and dried by N_2 gas gun. The substrates were treated by O_2 plasma treatment under the conditions of 2×10^{-2} Torr at $125\,W$ for $2\,min$ [22]. All organic materials and metal were deposited under high vacuum (5×10^{-7} Torr). The OLEDs were fabricated in the following sequence: ITO/N,N'-diphenyl-N,N'-(1-napthyl)-(1,1'-phenyl)-4,4'-diamine (NPB) ($50\,nm$)/9,10-di(2-naphthyl)anthracene (ADN): Blue dopant materials ($30\,nm$, 2%)/tris(8-hydroxyquinoline) aluminum (Alq$_3$) ($20\,nm$)/lithium quinolate (Liq) ($2\,nm$)/Al ($100\,nm$). The current density (J), luminance (L), luminous efficiency (LE), and CIE chromaticity coordinates of the OLEDs were measured with a Keithley 2400 and Chroma Meter CS-1000A. Electroluminance was measured using a Roper Scientific Pro 300i.

Results and Discussion

Figure 1 shows the molecular structures of the dopant compounds used in this study. Compounds **1–3** were synthesized *via* Suzuki cross-coupling reactions between 4-bromo-triphenylamine and corresponding arylanthracene boronic acid compounds with moderate yields. After conventional purifications such as column chromatography and recrystallization, the newly synthesized blue-emitting materials (**1–3**) were purified further by train sublimation at reduced pressure, below 10^{-3} torr, and fully characterized using ^{1}H- and ^{13}C-NMR, infrared (IR), and low- and high-resolution mass spectrometry. High-pressure liquid chromatography (HPLC) analysis revealed that the purity of the blue-emitting materials (**1–3**) was at least 99.0%.

Figure 2 shows the absorption (a) and emission (b) spectra of each of compounds **1–3** in CH$_2$Cl$_2$ solution. The photophysical data are summarized in Table 1. The absorption spectra have two major bands in the range of
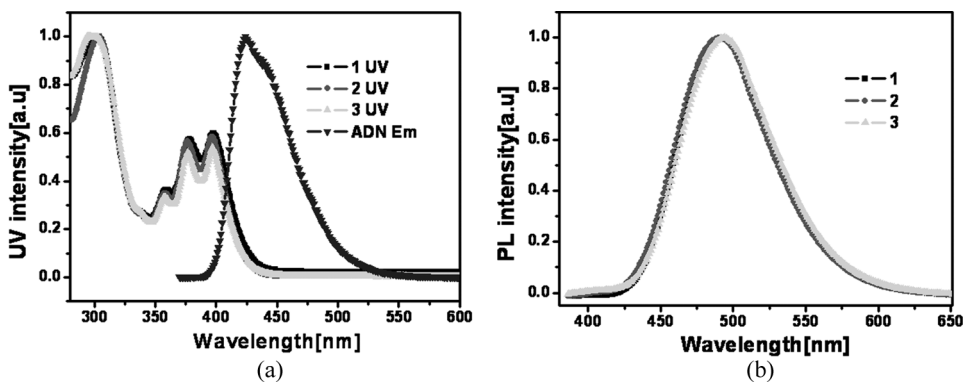
Figure 2. (a) The absorption and (b) emission spectra of compounds **1–3**.

Table 1. Optical properties of Compounds (**1–3**)

Compound	UV$_{max}$[a] [nm]	PL$_{max}$[b] [nm]	FWHM [nm]	HOMO/LUMO[c] [eV]	E$_g$	Φ[d]
1	397	492	74	5.71/2.82	2.89	0.67
2	396	492	50	5.75/2.83	2.92	0.72
3	397	494	75	5.63/2.68	2.95	0.72

[a,b]Maximum absorption or emission wavelength, measured in CH_2Cl_2 solution.
[c]Obtained from AC-2 and UV-vis absorption measurements.
[d]Using BDAVBi as a standard; $\lambda_{ex} = 360$ nm (Φ $= 0.86$ in CH_2Cl_2 solution).

360–400 nm. The peaks at 360–400 nm with a characteristic vibronic pattern are attributed to the π-π* transitions of the anthracene core [19,20]. The absorption bands at 280–350 nm can be interpreted as the combination of the n-π* transition of triaryl-amine moieties and the π-π* transitions of the substituted aryl groups on the anthra-cene core [21]. These compounds **1–3** all have similar emission properties in CH_2Cl_2 solution, each with a maximum peak at 492–494 nm, in the blue region. We calculated the fluorescence quantum yield (Φ) of **1–3** in the CH_2Cl_2 solution to be 0.67, 0.72 and 0.72, respectively, using BDAVBi (Φ $= 0.86$ in CH_2Cl_2 solution) as a standard [22], suggesting that these materials were expected to have highly efficient electrolumines-cent properties in OLED devices. Their full widths at half maximum (FWHM) were 74, 50 and 75 nm, respectively, in CH_2Cl_2 solution. The edge of the UV-Vis spectra was used to calculate the band gap of these blue materials. The calculated HOMO-LUMO energy gaps (E$_g$) for **1–3** were 2.89, 2.92, and 2.95 eV, respectively. The highest occupied molecular orbital (HOMO) levels were determined by using a photoelectron spectrometer (Riken-Keiki AC-2), and the lowest unoccupied mol-ecular orbital (LUMO) levels were calculated by subtracting the corresponding optical band gap energies from the HOMO values. The HOMO and LUMO energy levels for blue fluorescent materials varied from −5.63 to −5.75 eV and −2.68 to −2.83 eV, respectively (Table 1). In particular, the blue material dopant **1**, with a sub-stituted 2-naphthylanthracene unit had lower HOMO (−0.08 eV) and LUMO energy levels (−0.14 eV) in comparison with dopant **3**, with a substituted 1-naphthylanth-racene core. These results suggest that 2-position of naphthylanthracene group decreases the HOMO and LUMO energy levels through the effective π-conjugation.

The device performance of the blue fluorescent materials was studied by doping these materials in the ADN host at a 2% concentration. Figure 3 shows the device structure and relative HOMO/LUMO energy levels of the materials used in this study. NPB was employed as a hole-transporting layer (HTL) to provide hole trans-port, and also functioned as host in the emitting layer (EML), while Alq$_3$ was used as the electron-transporting layer (ETL) [23,24].

Figure 4 shows the EL emission spectra of the OLEDs obtained from devices **1–3**, and indicate that doped devices exhibited deeper blue than nondoped devices. All devices exhibited blue emissions with maximum emission peaks at 460, 456, and 458 nm for device **1**, **2**, and **3** (Table 2). Interestingly, there is a blue shift in EL spectra of the device **3** as compared to device **1**, because the steric effect of the 1-naphthalene group of dopant **3** decreases the π-conjugation length. The CIE (Commission Internationale de l'Eclairage) coordinates of devices **1–3** were (0.16, 0.17), (0.15, 0.14), and (0.15, 0.14), respectively, which were close to the NTSC
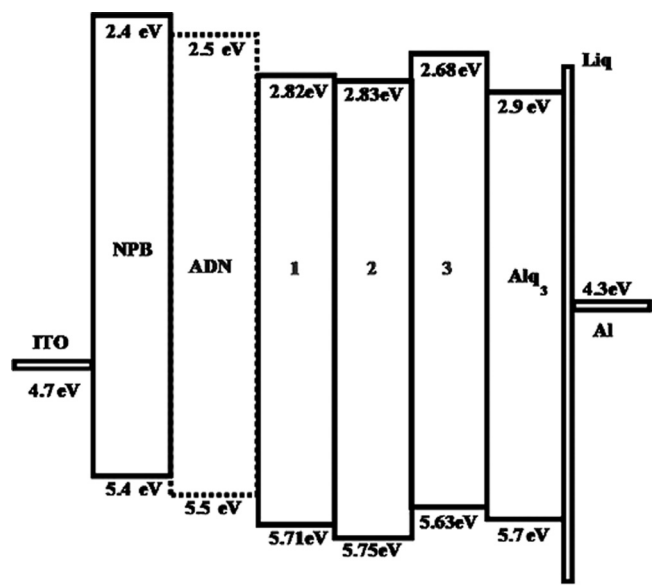
Figure 3. Energy-level diagram of the materials in devices **1**–**3**.

standard blue ($x = 0.15$, $y = 0.16$). However, the CIE coordinates of the nondoped devices corresponding to **1** and **2** were (0.14, 0.21), (0.14, 0.20) respectively, which indicates that the doped devices exhibited a deeper blue color than the nondoped device because the dopant materials functioned as a carrier trap in the doping system.

All devices **1**–**3** showed efficient blue emission, with results summarized in Table 2. The device **3**, which uses dopant **3** containing 1-naphtyl unit, exhibited CIE coordinates of (0.15, 0.14) at 12 V, a luminance of 7225 cd/m^2 at 12 V, a luminous efficiency of 4.62 cd/A, and a power efficiency of 1.81 lm/W at 20 mA/cm^2. Intriguing, similar results were obtained in the device **2** and **3**. In other words,
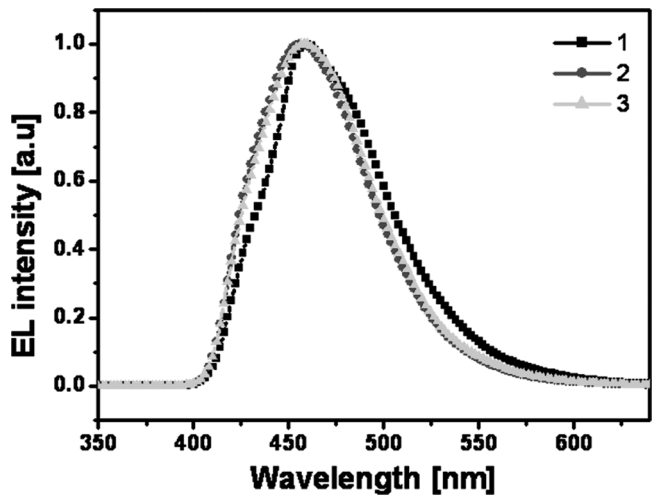

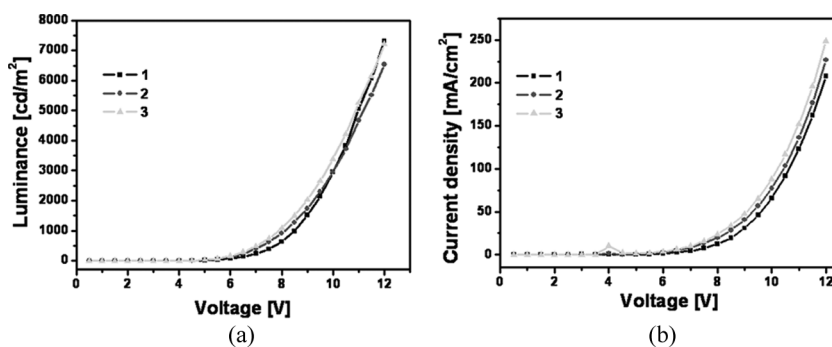**Figure 4.** Electroluminescence (EL) spectra of the devices **1**–**3**.

Figure 5. (a) *L-V* characteristics and (b) *I-V* characteristics of the devices **1–3**.
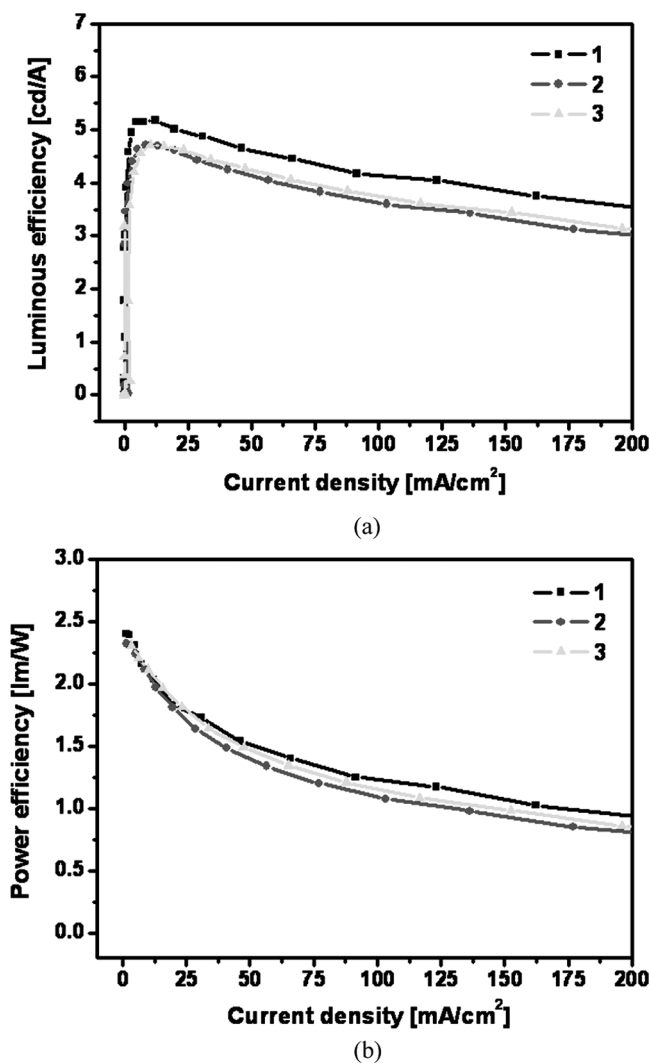

(a)

(b)

Figure 6. (a) Luminous and (b) Power efficiencies as a function of current density for the devices **1–3**.

Table 2. EL performance characteristic of devices (**1–3**)

Device	EL_{max}[a] [nm]	L[b] [cd/m^2]	LE[c] [cd/A]	Max LE[d] [cd/A]	PE[e] [lm/W]	Max PE[f] [lm/W]	CIE[a] (x, y)
1	460/472[g]	7306	4.95	5.18/5.5[g]	1.83	3.72/3.5[g]	(0.16, 0.17) (0.14, 0.21)[g]
2	456/470[g]	6541	4.61	4.71/4.0[g]	1.81	2.30/4.0[g]	(0.15, 0.14) (0.14, 0.20)[g]
3	458	7225	4.62	4.71	1.81	2.29	(0.15, 0.14)

Device (ITO/NPB/ADN: blue dopant materials **1–3** (2%)/Alq$_3$/Liq/Al).
[a]Value collected at 12.0 V.
[b]Maximum luminance at 12.0 V.
[c]Luminous efficiency at 20 mA/cm^2.
[d]Maximum luminous efficiency.
[e]Power efficiency at 20 mA/cm^2.
[f]Maximum power efficiency.
[g]Nondoped device with a configuration of ITO/NPB (50 nm)/EML/TPBI (30 nm)/LiF/ MgAg [17].

device **2**, employing compound **2** with a phenyl substituent as a dopant material, indicated deep blue emission with CIE coordinates of (0.15, 0.14) at 12.0 V, the maximum luminance of 6541 cd/m^2 at 12.0 V, and the luminous and power efficiencies of 4.61 cd/A and 1.81 lm/W at 20 mA/cm^2, respectively. The EL performances of devices **1–3** are sensitive to the structure of blue dopant materials in the emitting layer. Among those, a device using dopant **1** comprising 2-naphtyl moiety exhibited the best performance, with the maximum luminance of 7306 cd/m^2 at 12.0 V, and the luminous and power efficiencies of 4.95 cd/A and 1.83 lm/W at 20 mA/cm^2, respectively. However, the EL performances of the doped systems were not improved over those of undoped systems. This indicates that energy transfer between host (AND) and dopants (**1–3**) is not efficient because the absorption of dopants (**1–3**) do not overlap effectively with the emission of a common host (ADN) as shown in Figure 1 (a). This study implies that the effective energy transfer between host and dopant is a key factor in improving the EL performances in a doped system.

Conclusions

In conclusion, highly efficient blue dopant materials based on mono(triphenylamino) anthracene derivatives were synthesized *via* Suzuki cross-coupling. Multilayered OLEDs were fabricated with the device structure of ITO/NPB/2% anthracene-triphenylamine derivatives **1–3** doped in ADN/Alq$_3$/Liq/Al. All devices exhibited efficient blue emissions. Among those, device **1**, with CIE x, y coordinates of (0.16, 0.17) at 12.0 V, exhibited the best performance, with maximum luminance of 7306 cd/m^2 at 12.0 V, and luminous and power efficiencies of 4.95 cd/A and 1.83 lm/W at 20 mA/cm^2, respectively.

Acknowledgments

References

[1] Chen, C. H., Wu, F. I., Shu, C. F., Chen, C. H., & Tao, Y. T. (2004). *J. Mater. Chem.*, *14*, 1585.

[2] Tang, C. W., VanSlyke, S. A., & Chen, C. H. (1989). *J. Appl. Phys.*, *65*, 3610.

[3] Tang, C. W., & VanSlyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.

[4] Baldo, M. A., Thompson, M. E., & Forrest, S. R. (2000). *Nature*, *403*, 750.

[5] Adachi, C., Tsutsui, T., & Saito, S. (1989). *Appl. Phys. Lett.*, *55*, 1489.

[6] Wu, C. C., Lin, Y. T., Wong, K. T., Chen, R. T., & Chien, Y. Y. (2004). *Adv. Mater.*, *16*, 61.

[7] He, F., Tian, L., Xie, W., Li, M., Gao, Q., Hanif, M., Zhang, Y., Cheng, G., Yang, B., Ma, Y., Liu, S., & Shen, J. (2008). *J. Phys. Chem. C.*, *112*, 12024.

[8] Shia, J., & Tang, C. W. (2002). *Appl. Phys. Lett.*, *80*, 3201.

[9] Kim, Y. H., Shin, D. C., Kim, S. H., Ko, C. H., Yu, H. S., Chae, Y. S., & Kwon, S. K. (2001). *Adv. Mater.*, *13*, 1690.

[10] Li, Y., Fung, M. K., Xie, Z., Lee, S. T., Hung, L. S., & Shi, J. (2002). *Adv. Mater.*, *14*, 1317.

[11] Danel, K., Huang, T. H., Lin, J. T., Tao, Y. T., & Chuen, C. H. (2002). *Chem. Mater.*, *14*, 3860.

[12] Shen, W. J., Dodda, R., Wu, C. C., Wu, F. I., Liu, T. S., Chen, H. H., Chen, C. H., & Shu, C. F. (2004). *Chem. Mater.*, *16*, 930.

[13] Kan, Y., Wang, L., Duan, L., Wu, G., & Qiu, Y. (2004). *Synth. Met.*, *141*, 245.

[14] Gebeyehu, D., Walzer, K., He, G., Pfeiffer, M., Leo, K., Brandt, J., Gerhard, A., Stoessel, P., & Vestweber, H. (2005). *Synth. Met.*, *148*, 205.

[15] Kim, Y. H., Jeong, H. C., Kim, S. H., Yang, K., & Kwon, S. K. (2005). *Adv. Funct. Mater.*, *15*, 1799.

[16] Lyu, Y. Y., Kwak, J., Kwon, O., Lee, S. H., Kim, D., Lee, C., & Char, K. (2008). *Adv. Mater.*, *20*, 2720.

[17] Tao, S., Zhou, Y., Lee, C. S., Lee, S. T., Huang, D., & Zhang, X. (2008). *J. Phys. Chem. C.*, *112*, 14603.

[18] Kauffman, J. M., & Moyna, G. (2003). *J. Org. Chem.*, *68*, 839.

[19] Lee, J. H., Ho, Y. H., Lin, T. C., & Wu, C. F. (2007). *J. Elect. Soc.*, *154*, J226.

[20] Wang, X., Chen, J., You, H., Ma, D., & Sun, R. (2005). *Jpn. J. Appl. Phys.*, *44*, 8480.

[21] Kim, S. K., Park, J. W., & Oh, S. Y. (2007). *Mol. Cryst. Liq. Cryst.*, *471*, 89.

[22] Li, C. L., Shieh, S. J., Lin, S. C., & Liu, R. S. (2003). *Org. Lett.*, *5*, 1131.

[23] Hung, L. S., & Chen, C. H. (2002). *Mater. Sci. Eng. R*, *39*, 143.

[24] Lia, M., Li, W., Sua, W., Zanga, F., Chua, B., Xina, Q., Bia, D., Lia, B., & Yua, T. (2008). *Solid-State Electronics*, *52*, 121.