Article

Journal of
Nanoscience and Nanotechnology
Vol. 15, 1850–1854, 2015
www.aspbs.com/jnn

New Approach Way Using Substituent Group at Core Chromophore for Solution Process Blue Emitter

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Comparing the conventional vapor desposition process for OLEDs, the solution process using small molecules has merits of low production cost because of many reasons. For the solution process blue flourescent material, tertiary butyl (T) and anthracene (A) were first introduced as substituents to TAT core part, 2-tert-butyl-9,10-bis(3″,5″-diphenylbiphenyl-4′-yl)anthracene (T-TAT) and 2-(9-anthracenyl)-9,10-bis(3″,5″-diphenylbiphenyl-4′-yl)anthracene (A-TAT). All three materials indicated typical absorption band of anthracene in the range of 350 to 400 nm. T-TAT exhibited similar optical properties to TAT, but A-TAT has longer absorption and PL emission compared to other two compounds. In case of spin-coated film, A-TAT exhibited absorption maximum value of 408 nm and photoluminescence maximum value of 469 nm. T-TAT and A-TAT can be applicable to solution process as a blue fluorescence material.

Keywords: OLEDs, Solution Process, Blue Fluorescent Emitter.

1. INTRODUCTION

Small organic molecules based organic light emitting diodes (OLEDs) are under many intense researches in view of their promising future for large full color display applications such as TV and advertising displays. OLED has been under active researches so far with its overlooking high potential for use in liquid crystal display (LCD) backlight and lighting field due to its low power consumption.[1–4]

Small molecule based OLED device (SMOLED) has been already commercialized in mobile phone due to its high efficiency compared to polymer based OLED device (PLED).

Nevertheless, SMOLED has a problem of high cost as it utilizes a deposition method, which involves high cost for deposition equipment and large consumption of material.[5–8] Thus, to solve high cost and large size panel production problem, OLED is widely researched by using a solution process such as ink-jet printing, nozzle printing, and spin-coating that uses a simple device structure and consumes less material.[9–12]

Materials applied to SMOLED have been mainly developed for a deposition process so far. However, a deposition method and a solution process require very different material characteristics. Therefore, development of small molecule material that is suitable for a solution process is necessary. A research on small molecule emitting materials which is available for solution process is very important for implementation of OLED.

As for the solution process, emitting materials are required to be soluble, which means that compound should break packing property inside of molecule itself.

In this study, we propose new approach method to prevent packing of chromophores by introducing alkyl or aromatic moiety into main chromophore. In our previous paper, 9,10-bis(3″,5″-diphenylbiphenyl-4′-yl)anthracene (TAT),[13] a blue fluorescent emitter was shown to have high efficiency through the deposition process. In here, we changed main core part using tertiary butyl or another anthracene group as shown in Figure 1 and characterized new compounds.

2. EXPERIMENTAL DETAILS

2.1. General Experiment

^{1}H-NMR spectra were recorded on Bruker, Advance 300, while Fast atom bombardment (FAB) mass spectra were recorded by JEOL, JMS-AX505WA, HP5890 series II. The elementary analysis (EA) was checked by EA1110 and EA1112 of CE Instruments. The optical absorption spectra were obtained by HP 8453 UV-VIS-NIR

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1533-4880/2015/15/1850/005 doi:10.1166/jnn.2015.9299

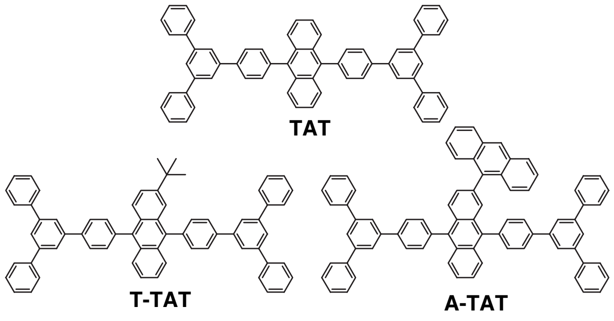


Figure 1. Chemical structures of TAT, T-TAT and A-TAT.

spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photoluminescence (PL) spectroscopy. HOMO values were measured by RIKEN Surface analyzer AC-2. The melting temperatures (T_m) and glass-transition temperatures (T_g) of the compounds were measured by carrying out differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC4000 (Perkin Elmer).

Thin film was prepared by spin-coating of the synthesized compound solution (1.5 wt%, toluene) with 15 seconds of 1000 rpm and 15 seconds of 2000 rpm. The film was baked for 30 min at 70 °C by using a hot plate to remove the solvent. All deposited films were thermally evaporated on the substrates in a vacuum of less than 1×10^{-6} torr at an evaporation rate of 1 Å/s. Film thickness was measured by using an Alpha-step 500 surface profiler (KLA Tencor, Mountain View, CA).

2.2. Synthesis of Compound 1

The method of synthesis for Compound 1 in Scheme 1 is published in Chem. Mater.[14]

2.3. Synthesis of Compound 2

The method of synthesis for Compound 2 in Scheme 1 is published in J. Mater. Chem. C.[13]

2.4. Synthesis of 2-Tert-Butyl-9,10-Bis(3″,5″4-diphenylbiphenyl-4′-yl)Anthracene (T-TAT)

Compound 1 (3.0 g, 5.5 mmol) and compound 2 (3.3 g, 12.1 mmol) were added to Pd(OAc)$_2$ (50 mg, 0.22 mmol), tris(2-methylphenyl)phosphine (155 mg, 0.44 mmol), K_3PO_4 (9.4 g, 44 mmol), and solvent (dimethoxyethane:water = 4:1) in a 500 mL round-bottomed flask under a nitrogen atmosphere. The temperature was raised to 100 °C. When the reaction was completed, extraction of the product was performed with water and chloroform. The organic extract was dried with added $MgSO_4$ and then filtered. The solvent was removed under vacuum. The remaining crude mixture was passed through a column of silica with MC:Hexane (1:5) and then re-crystallized from chloroform to obtain a yellow solid. The final step yield was 73%.

^{1}H-NMR (300 MHz, $CDCl_3$)δ(ppm): 8.01–7.94 (*m*, 8 H), 7.87 (*t*, 2 H), 7.83–7.79 (*m*, 6 H), 7.77 (*s*, 5 H), 7.73 (*d*, 1 H), 7.64–7.60 (*m*, 4 H), 7.55–7.48 (*m*, 9 H), 7.45–7.39 (*m*, 4 H), 7.38–7.25 (*m*, 2 H), 1.29 (*s*, 9 H). Fab$^+$-MS 963 m/z. Anal. Calcd for C66H50: C, 94.02; H, 5.98 Found: C, 93.98; H, 5.88.

2.5. Synthesis of Compound 3

The method of synthesis for Compound 3 in Scheme 1 is published in Angew. Chem.[15]

2.6. Synthesis of Compound 4

The method of synthesis for Compound 4 in Scheme 1 is published in J. Mater. Chem. C.[13]

2.7. Synthesis of Compound 5

In a 500 mL round-bottomed flask, Compound 3 (0.5 g, 1.76 mmol), Compound 4 (0.58 g, 2.64 mmol), Pd(OAc)$_2$ (11.8 mg, 0.05 mmol) and tricyclohexylphosphine (29.5 mg, 0.1 mmol) were placed with Anhydrous Toluene and Ethanol. It was raised to 110 °C and (Et)$_4$NOH was added to reaction flask. After reaction is completed, it is extracted by Chloroform and water. After removing water from the mixture, it was filtered by using $MgSO_4$. The mixture was columned under MC:Hexane (1:4) mixed solvent. The product was concentrated under reduced pressure and re-precipitated with methanol to obtain pure solid material. The yield was 59%.

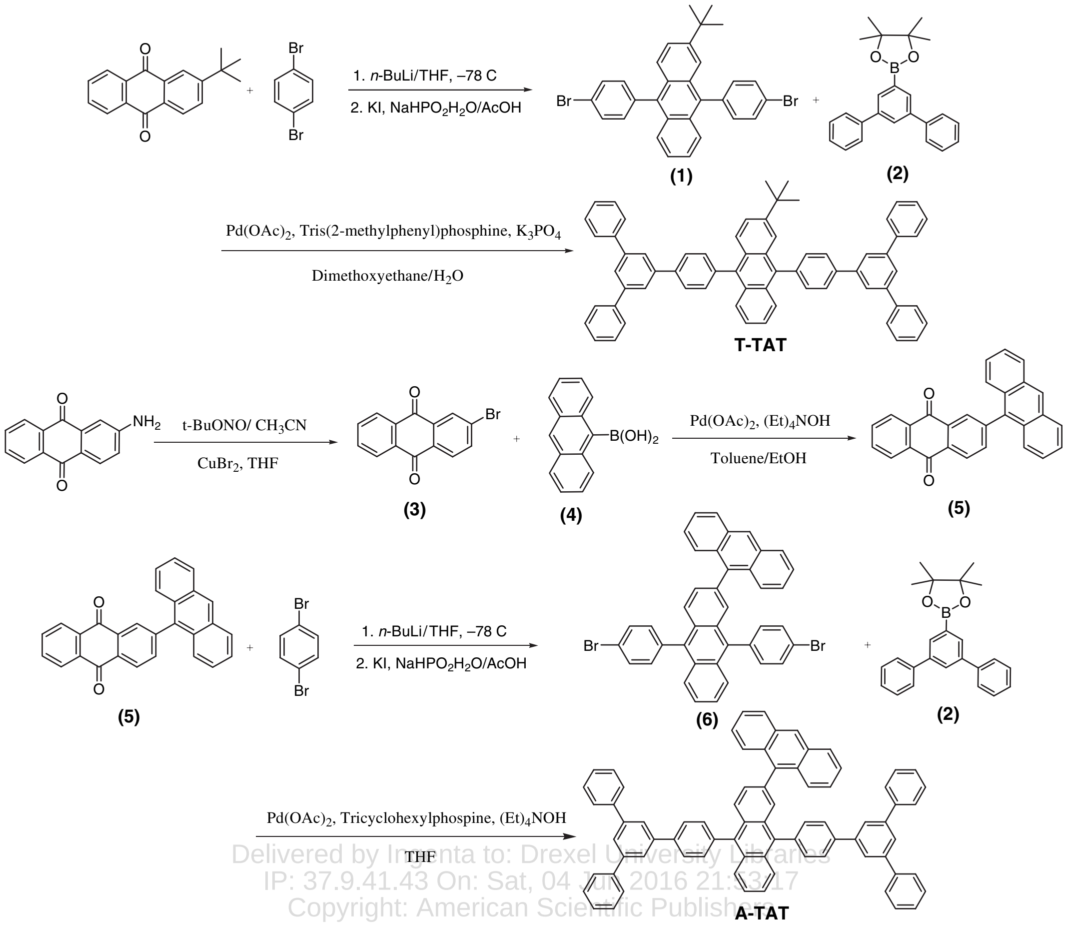
2.8. Synthesis of Compound 6

The method of synthesis for Compound 1 in Scheme 1 is published in Chem. Mater.[14]

2.9. Synthesis of 2-(9-anthracenyl)-9,10-Bis(3″,5″-diphenylbiphenyl-4′-yl)Anthracene (A-TAT)

In a 250 mL round-bottomed flask, compound 6 (1.4 g, 2.10 mmol), compound 2 (1.876 g, 5.26 mmol), Pd(OAc)$_2$ (113.5 mg, 0.17 mmol), and tricyclohexylphosphine (94 mg, 0.34 mmol) were placed with anhydrous THF solvent. It was raised to 80 °C and (Et)$_4$NOH was added to reaction flask. After reaction is completed, it is extracted by chloroform and water. After removing water from the mixture, it was filtered by using $MgSO_4$. The mixture was columned under EA:Hexane (1:10) mixed solvent. The product was concentrated under reduced pressure and re-precipitated with methanol to obtain pure solid material in light yellow color. The final step yield was 49%.

^{1}H-NMR (300 MHz, THF) δ(ppm): 8.53–8.50 (*s*, 1 H), 8.18–8.12 (*d*, 2 H), 8.12–8.08 (*d*, 2 H), 8.08–8.00 (*m*, 3 H), 7.98–7.93 (*m*, 3 H), 7.93–7.86 (*m*, 6 H), 7.86–7.82 (*m*, 4 H), 7.79–7.68 (*m*, 8 H), 7.67–7.62 (*d*, 2 H), 7.53–7.46 (*m*, 5 H), 7.46–7.36 (*m*, 10 H), 7.34–7.28 (*m*, 4 H). Fab$^+$-MS 963 m/z. Anal. Calcd for C76H50: C, 94.77; H, 5.23 Found: C, 94.67; H, 5.23.



Scheme 1. Synthetic routes of T-TAT and A-TAT.

3. RESULTS AND DISCUSSION

In blue fluorescence compound, it generally has core and side moieties. For example, anthracene is core part and triphenyl group is two side groups in TAT chemical structure as shown in Figure 1. TAT can basically emits from core part and it can be tuned by side moiety.[13] As we mentioned in introduction part, we modified chemical structures at #2 position of antracence core part in order to break molecule packing and be available for solution process by using two big size chemical groups such as tertiary butyl (*t*-butyl) and anthracene.

Figure 2 shows UV-visible (UV-Vis.) absorption and PL spectra of three compounds in solution state and film state. Film was prepared by evaporation (Fig. 2(b)) and spin coating (Fig. 2(c)) methods.

Optical properties of two new synthesized materials were different. T-TAT exhibited similar property with unmodified compound of TAT but A-TAT showed relatively longer PL maximum wavelength.

Those data are summarized in Table I. Absorption in solution state of three compounds shows the typical anthracene absorption band in the range of 350 to 400 nm and major peaks of 376 nm, 376 nm and 386 nm, respectively.

The absorption edge for A-TAT starts at longer wavelengths compared with TAT or T-TAT. Therefore, the band gap for A-TAT is reduced compared with that of TAT or T-TAT. This is caused by an increase in conjugation length from the anthracene introduced as a substituent. As shown in the PL spectrum of solution state, TAT, T-TAT and A-TAT have maximum values at 436 nm, 439 nm and 451 nm, respectively. As for A-TAT, since the conjugation length is increased by substituted anthracene to main core, emission value is located at longer wavelength compared to TAT or T-TAT.

From Figure 2(b) data, similar results were obtained, but A-TAT had vivid excimer band at 525 nm in PL spectrum. It means that A-TAT compound can produce another interaction between molecules when it was evaporated due to the second anthracene moiety at core part. Thus, in evaporation case, it can cause partially limitation and disadvantage to introduce another aromatic group although it has large size because excimer band decrease the efficiency and color purity.

Figure 2(c) and Table I exhibit the spin coating film data. PL maximum values of TAT, T-TAT and A-TAT are 451 nm, 452 nm, and 469 nm. A-TAT has red-shifted data value. Since the film condition is closer in separation

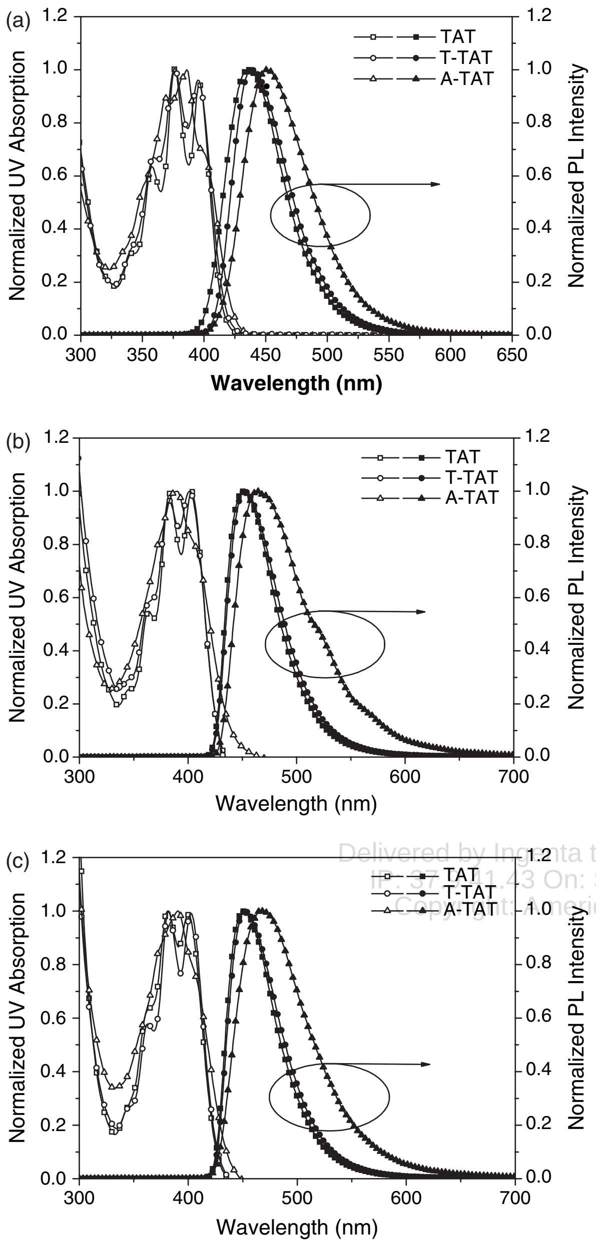


Figure 2. UV-visible absorption and PL spectra of TAT (square), T-TAT (circle) and A-TAT (triangle): (a) solution in chloroform (1.0×10^{-5} M), (b) evaporation film, (c) spin-coated film.

of distances between molecules compared to the solution state, it can be seen that the UV absorption peaks have red-shifted approximately 4∼8 nm and the emission peaks between 13∼18 nm. Interestingly, A-TAT does not show excimer band at 525 nm in spin-coated film. It may be prevented to interact anthracene each other in spin-coated film.

CIE values of the devices including TAT, T-TAT, and A-TAT emitting layer were (0.150, 0.097), (0.147, 0.097), and (0.180, 0.250) at 20 mA/cm^2.

HOMO values for the TAT, T-TAT and A-TAT were measured by AC-2 at 5.62 eV, 5.62 eV, 5.65 eV, respectively. It was verified that when tertiary butyl or anthracene substituent group added to the TAT, HOMO values would not significantly change. LUMO values of 2.68, 2.71, and 2.84 eV for the TAT, T-TAT, and A-TAT were calculated from the band gap energy. We carried out DSC analyses to determine the thermal properties of the synthesized compounds. All of TAT, T-TAT and A-TAT have high T_g values above 150 °C. TAT exhibited T_m of 340 °C and T-TAT and A-TAT didn't show T_m values. Those data are summarized in Table II.

Table I. Optical properties of synthesized materials.

	Solution^a		Film^b		Film^c	
Compound	UV$_{max}$ (nm)	PL$_{max}$ (nm)	UV$_{max}$ (nm)	PL$_{max}$ (nm)	UV$_{max}$ (nm)	PL$_{max}$ (nm)
TAT	358, 376, 396	436	383, 403	451	382, 400	451
T-TAT	359, 376, 395	439	383, 402	452	382, 402	452
A-TAT	369, 386, 400	451	390, 406	464, 525	391, 408	469

Notes: ^{a}Chloroform solution (1×10^{-5} M); ^{b}deposited film; ^{c}spin coating film.

Table II. Electrical and thermal properties of the synthesized compounds.

Compound	HOMO (eV)	LUMO (eV)	Band gap (eV)	T_g (°C)	T_m (°C)
TAT	5.62	2.68	2.94	150	340
T-TAT	5.62	2.71	2.91	163	–
A-TAT	5.65	2.84	2.81	194	–

4. CONCLUSION

Tertiary butyl and anthracene groups were introduced as substituents to the anthracene core part of TAT in order to be available for solution process blue emitter.

T-TAT exhibited similar optical properties with TAT. However, A-TAT showed relatively longer absorption and emission in solution as well as film state. In case of A-TAT, excimer band was shown in deposition film, but no excimer band at spin-coated film. It may be prevented to interact anthracene each other in spin-coated film. T-TAT and A-TAT can be applicable to solution process as a blue fluorescence material.

Acknowledgments: This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2012001846).

References and Notes

1. L. Ruppel, S. Mogck, and C. May, *IWFPE 2009*, Invited 6.1 **(2009)**.
2. W. Y. Lai, J. Levell, A. Jackson, S. C. Lo, P. Bernhardt, I. W. Samuel, and P. Burn, *Macromolecules* 43, 6986 **(2010)**.
3. Y. I. Park, B. J. Lee, K. H, J. H. Lee, S. Y. Oh, and J. W. Park, *J. Nanosci. Nanotechnol.* 12, 4325 **(2012)**.
4. S. H. Kim, K. J. Lee, B. J. Kim, J. H. Lee, K. Y. Kay, and J. W. Park, *J. Nanosci. Nanotechnol.* 13, 8020 **(2013)**.

5. J. Intemann, J. Mike, M. Cai, S. Bose, T. Xiao, T. Mauldin, R. Roggers, J. Shinar, R. Shinar, and M. EL, *Macromolecules* 44, 248 (**2011**).
6. H. Kim, Y. Byun, R. R. Das, B. K. Choi, and P. S. Ahn, *Appl. Phys. Lett*. 91, 093512 (**2007**).
7. N. C. Yang and M. C. Suh, *Curr. Appl. Phys*. 9, 505 (**2009**).
8. D. H. Hwang, J. D. Lee, M. J. Lee, and C. H. Lee, *Curr. Appl. Phys*. 5, 244 (**2005**).
9. S. H. Jung and J. J. Kim, *IWFPE 2009*, Invited 7.3 (**2009**).
10. S. C. Chang, J. Liu, J. Bharathan, Y. Yang, J. Onohara, and J. Kido, *Adv. Mater*. 11, 734 (**1999**).
11. D. H. Lee, J. H. Park, H. Chae, and S. M. Cho, *Organic Electronics* 10, 1345 (**2009**).
12. D. H. Lee, J. S. Choi, H. Chae, C. H. Chung, and S. M. Cho, *Curr. Appl. Phys*. 9, 161 (**2009**).
13. S. K. Kim, B. Yang, Y. Ma, J. H. Lee, and J. W. Park, *J. Mater. Chem*. 18, 3376 (**2008**).
14. K. Danel, T. H. Huang, J. T. Lin, Y. T. Tao, and C. H. Chuen, *Chem. Mater*. 14, 3860 (**2002**).
15. K. Ito, T. Suzuki, Y. Sakamoto, D. Kubota, Y. Inoue, F. Sato, and S. Tokito, *Angew. Chem.* 115, 1191 (**2003**).

Received: 14 June 2013. Accepted: 24 September 2013.