

Simple modification of anthracene for the blue emitting materials

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Abstract : Anthracene has been a motive molecule for the blue-emitting materials in OLED. Since the blue emission needs big band gap between HOMO and LUMO, the blue-emitting materials are rare. In this paper, some anthracene derivatives containing simple aryl groups are synthesized and characterized. Regardless of the substituents the absorption and the emission bands are similar to each other and similar to the derivatives with the bulky silyl groups. The thermal and the CIE tests imply that among the tested 9-(2-naphthyl)-10-phenylanthracene is most promising for the diode. The material for the emission layer has to be investigated, which is simple to be prepared as well as good in the electrical and the thermal properties.

Keywords : deep-blue emission, anthracene, synthesis, OLED, excimer

1. Introduction

Since Tang et.al. have reported the possibility of a flat panel display, OLED, a lot of materials and systems have been studied and developed [1-3]. There must be many layers like hole transporting, electron transporting, hole blocking, electron blocking, and emission layers in order to composite the diodes. Full color display essentially needs red, green, and blue color emitting materials. While the red and the green color emitting materials have shown sufficient efficiency and life time for OLED, the blue color emitting materials have not shown the satisfactory data yet, due to the wide band gap. Therefore, the research of the blue color emitting materials has aimed

to the longer life time and the purer color emission [4-6]. The blue emitting materials have been studied such as carbazole (λ_{em} :344 nm) [7], fluorathene (368 nm) [8], fluorene (415 nm) [9], and anthracene (396 nm) [10,11]. Some blue color emitting materials are synthesized including anthracene as a backbone because of brightly emitting characteristics by itself.

Since the hydrogen of anthracene are labile at the 9- and 10-positions they would be substituted more easily than the other ones [12]. Therefore, the derivatives of anthracene could be the good candidates for the blue color emitting material due to the color fidelity as well as the simple preparation.

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2. Experimental details

2.1. Materials

9,10-Dibromoanthracene, phenyl boronic acid, p-tolyl boronic acid, 4-(trifluoromethyl) phenyl boronic acid, 1-naphthyl boronic acid, 2-naphthyl boronic acid, tetrakis(triphenylphosphine)palladium were purchased from Sigma Aldrich Korea Co.

2.2. Synthesis and characterization

Suzuki cross coupling reaction has been applied throughout all the procedure under N₂. ¹H- and ¹³C- NMR were measured on JNM-Lambda series Zeol Co in CDCl₃. Low resolution mass spectroscopy were measured by 5973N Mass selective detector. Elemental analysis was carried out on a FLASH EA-2000 Thermo scientific Co.

2.2.1. 9-bromo-10-phenylanthracene (BPA, **1**)

9,10-Dibromoanthracene (2.98 mmol) and phenyl boronic acid (2.98 mmol) were mixed in THF. 2 M K₂CO₃ aqueous solution (50 ml) and tetrakis(triphenylphosphine)palladium (0.1 mmol) were added to the mixture. The resultant solution was refluxed for 8hr at 60°C. After cooling, the mixture was worked up, purified by column chromatography, and recrystallized in methanol to get yellow solid (58%). ¹H-NMR (CDCl₃); 8.54 (d, 2H), 7.52 (m, 7H), 7.31 (m, 4H); ¹³C-NMR (CDCl₃); 138.3, 137.7, 131.1, 131.0, 130.19, 128.4, 127.8, 127.7, 127.3, 126.9, 125.5, 122.7.

2.2.2. 9,10-diphenylanthracene (DPA, **2**)

Phenyl boronic acid (2.98 mmol) was added to BPA (**1**). The synthetic procedure was similar to the one of **1**. Yellow solid (87%) was obtained. ¹H-NMR (CDCl₃); 7.62 (m, 4H), 7.52 (m, 6H), 7.42 (m, 4H), 7.26 (m, 4H); ¹³C-NMR (CDCl₃); 139.0, 137.0, 131.3, 129.8, 128.4, 127.4, 126.9, 124.9.

2.2.3. 9-(1-naphthyl)-10-phenylanthracene (1-NPA, **3**)

The synthetic procedure of 1-NPA (**3**) was similar to the one of **1** except 1-naphthyl boronic acid (2.98 mmol) instead of phenyl boronic acid. Yellow solid (83%) was obtained. ¹H-NMR (CDCl₃); 7.97 (m, 2H), 7.65 (m, 3H), 7.51 (m, 6H), 7.39 (t, 3H), 7.25 (m, 2H), 7.18~7.09 (m, 4H); ¹³C-NMR (CDCl₃); 139.0, 137.4, 136.7, 134.9, 133.6, 133.5, 131.3, 130.6, 129.8, 128.4, 128.2, 128.1, 127.4, 126.6, 126.2, 125.9, 125.5, 127.0, 125.1, 125.0.

2.2.4. 9-(2-naphthyl)-10-phenylanthracene (2-NPA, **4**)

The synthetic procedure of 2-NPA (**4**) was similar to the one of **3** except 2-naphthyl boronic acid (2.98 mmol) instead of 1-naphthyl boronic acid to get white solid (87%). ¹H-NMR (CDCl₃); 7.98 (m, 4H), 7.70 (m, 4H), 7.59 (m, 6H), 7.49 (t, 2H), 7.35~7.26 (m, 4H); ¹³C-NMR (CDCl₃); 139.0, 137.2, 136.8, 136.6, 133.4, 132.7, 131.3, 130.2, 130.0, 129.9, 129.5, 128.4, 128.0, 127.9, 127.4, 127.0, 126.4, 126.2, 125.0; MS: m/z 380 (M⁺ for C₂₆H₂₀); Anal calcd for C₂₆H₂₀; C, 94.7; H, 5.3. Found: C, 94.0; H, 5.3.

2.2.5. 9-phenyl-10-(p-tolyl)anthracene (PTA, **5**)

The synthetic procedure of PTA (**5**) was similar to the one of **2** except p-tolyl boronic acid (2.98 mmol) to get yellow solid (95%). ¹H-NMR (CDCl₃); 7.68(m, 4H), 7.53(m, 4H), 7.39(t, 4H), 7.34~7.27(m, 4H), 2.53(s, 3H); ¹³C-NMR (CDCl₃); 139.1, 137.2, 137.0, 136.9, 135.9, 131.3, 131.1, 129.9, 129.8, 129.1, 128.3, 127.4, 127.0, 126.9, 124.9, 124.8, 21.5; MS: m/z 344(M⁺ for C₂₇H₂₀); Anal calcd for C₂₇H₂₀; C, 94.1; H, 5.9. Found: C, 92.7; H, 5.80.

2.2.6. 9-(1-naphthyl)-10-(p-tolyl)anthracene (1-NTA, **6**)

The synthetic procedure of 1-NTA (**6**) was similar to the one of **3** except p-tolyl boronic acid (2.98 mmol) to get a yellow solid (91%). ¹H-NMR (CDCl₃): 8.02 (m, 2H), 7.77~7.66 (m, 3H) 7.55 (d, 1H), 7.49~7.38 (m, 7H), 7.29 (m, 2H), 7.18 (m, 4H), 2.54 (s, 3H); ¹³C-NMR (CDCl₃): 137.5, 137.1, 136.8, 135.9, 134.8, 133.6, 133.5, 131.2, 130.6, 130.0, 129.2, 129.1, 128.2, 128.0, 127.1, 127.0, 126.6, 126.2, 125.9, 125.5, 125.1, 124.9, 21.4; MS: m/z 394 (M⁺ for C₃₁H₂₂); Anal calcd for C₃₁H₂₂; C, 94.4; H, 5.6. Found: C, 93.6; H, 5.7.

2.2.7. 9-(2-naphthyl)-10-(p-tolyl)anthracene (2-NTA, **7**)

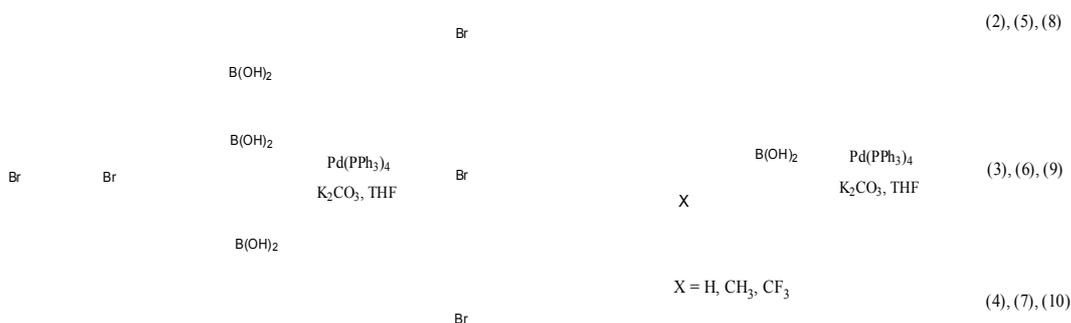
The synthetic procedure of 1-NTA (**7**) was similar to the one of **4** except p-tolyl boronic acid (2.98 mmol) to get white solid (92%). ¹H-NMR (CDCl₃): 7.93 (m, 4H), 7.66 (m, 4H), 7.54 (m, 3H), 7.30 (m, 8H), 2.49 (s, 3H); ¹³C-NMR (CDCl₃): 137.3, 137.0, 136.6, 135.9, 133.3, 132.7, 131.1, 130.2, 130.0, 129.9, 129.5, 129.1, 128.0, 127.9, 127.8, 127.1, 126.9, 126.3, 126.1, 125.0, 124.9, 21.5; MS: m/z 394 (M⁺ for C₃₁H₂₂); Anal calcd for C₃₁H₂₂; C, 94.4; H, 5.6. Found: C, 91.9; H, 5.5.

2.2.8. 9-phenyl-10-(4-(trifluoromethyl)phenyl)anthracene (PFTA, **8**)

The synthetic procedure of PFTA (**8**) was similar to the one of **5** except 4-(trifluoromethyl)phenyl boronic acid (2.98 mmol) to get white solid (82.7%). ¹H-NMR (CDCl₃): 7.86 (d, 2H), 7.69 (m, 2H), 7.62~7.54 (m, 7H), 7.46 (t, 2H), 7.34 (m, 4H); ¹³C-NMR (CDCl₃): 138.7, 137.6, 135.1, 131.7, 131.2, 129.7, 129.5, 128.4, 127.5, 127.1, 126.3, 125.4, 125.1; MS: m/z 398 (M⁺ for C₂₇H₁₇F₃); Anal calcd for C₂₇H₁₇F₃; C, 81.4; H, 4.30. Found: C, 79.7; H, 4.27.

2.2.9. 9-(1-naphthyl)-10-(4-(trifluoromethyl)phenyl)anthracene (1-NFTA, **9**)

The synthetic procedure of 1-NFTA (**9**) was similar to the one of **6** except 4-trifluoromethylphenyl boronic acid (2.98 mmol) to get white solid (91.4%). ¹H-NMR (CDCl₃): 8.04 (m, 2H), 7.89 (t, 2H), 7.66 (m, 5H), 7.49 (m, 4H), 7.36~7.31 (m, 2H), 7.21 (m, 3H), 7.13 (d, 1H); ¹³C-NMR (CDCl₃): 136.4, 135.8, 133.4, 131.8, 131.7, 130.8, 130.5, 129.6, 129.1, 128.7, 128.2, 128.2, 127.8, 127.7, 127.2, 126.5, 126.4, 126.3, 126.0, 125.9, 125.5, 125.2; MS: m/z 448 (M⁺ for C₃₁H₁₉F₃); Anal calcd for C₃₁H₁₉F₃; C, 83.0; H, 4.3. Found: C, 80.6; H, 4.39.



Scheme 1. Synthetic routes of compounds 2~10.

2.2.10. 9-(2-naphthyl)-10-(4-(trifluoromethyl)phenyl)anthracene (2-NFTA, **10**)

The synthetic procedure of 2-NFTA (**10**) was similar to the one of **7** except 4-(trifluoromethyl)phenyl boronic acid (2.976 mmol) to get white solid (90%). ¹H-NMR (CDCl₃): 8.04 (m, 2H), 7.91 (m, 4H), 7.72 (d, 2H), 7.61 (m, 7H), 7.37~7.28 (m, 4H); ¹³C-NMR (CDCl₃): 133.4, 133.3, 132.7, 131.7, 130.1, 129.9, 129.6, 129.3, 128.0, 127.9, 126.4, 126.3, 126.2, 125.5, 125.2; MS: m/z 448 (M⁺ for C₃₁H₁₉F₃); Anal calcd for C₃₁H₁₉F₃: C, 83.0; H, 4.3. Found: C, 81.7; H, 4.2.

2.3. Physical measurements

Absorption and Florescence spectra were measured in cyclohexane using Evolution 60s and Cary Eclipse respectively. Thermogravimetric analysis was conducted using N-1000 system at a heating rate of 10°C/min from 25 to 500°C.

3. Results and discussion

The general synthetic route to the nine compounds are shown in Scheme 1, applying Suzuki Cross Coupling reactions. Commercialized BPA (**1**), DPA (**2**), 1-NPA (**3**), 2-NPA (**4**) have been synthesized.

The naphthyl group substitution of anthracene prior to the phenyl group results in better yield than the reverse (phenyl

substitution prior to the naphthyl) by 58% vs. 83%.

The UV-vis absorption spectra are shown in Figure 1 and summarized in Table 1. Three major bands of anthracene (λ_{\max} : 340 nm, 356 nm, 379 nm) are bathochromic-shifted in all the compounds (**2~10**).

The PL spectra are shown in Fig 2. and summarized in table 1. The emission bands of all the compounds have three bands similar to anthracene. However intensity ratios are different depending on the substituents. The ones with 2-naphthyl group have stronger emission in higher energy (~430 nm) than with phenyl or 1-naphthyl, which result in deeper blue emission referred from C.I.E. data (Table 2), regardless of the substituents at the other side: comparing the compounds of **2, 5, 8** and **3, 6, 9** with **4, 7, 10**.

As concentrated, the PL bands of the solution are shifted to the longer wavelength indicating existence of the excimer (Figure 3). The melting points of the compounds (303~333°C) implicate thermal stability in OLED [13].

The C.I.E data shown in Table 2 suggest all the compounds are suitable for the blue emitters. 2-Naphthyl derivatives shows deeper blue than the other ones, even the derivative with a triphenylsilane [14].

Table 1. Spectral and physical properties of compounds.

| Compound | UV λ_{\max} nm ^(a) | PL λ_{\max} nm ^{(a)(b)} | C.I.E ^(c) | T _m | E _g eV ^(d) |
|--------------------|---------------------------------------|--|----------------------|----------------|----------------------------------|
| Anthracene | 340/356/379 | 400/ - | - | 215.7 | 3.72 |
| PTA (5) | 355/373/395 | 430/444 | (0.17,0.16) | 306.1 | 3.04 |
| 1-NTA (6) | 355/375/394 | 430/447 | (0.16,0.14) | 303.5 | 3.05 |
| 2-NTA (7) | 355/374/395 | 433/451 | (0.15,0.12) | 306.2 | 3.02 |
| Reference [14] | 355/377/395 | 428/452 | (0.16,0.10) | - | 3.08 |

(a) In Cyclohexane. (b) Solid PL emission. (c) At 6V. (d) Energy level measured by absorption edge [16]

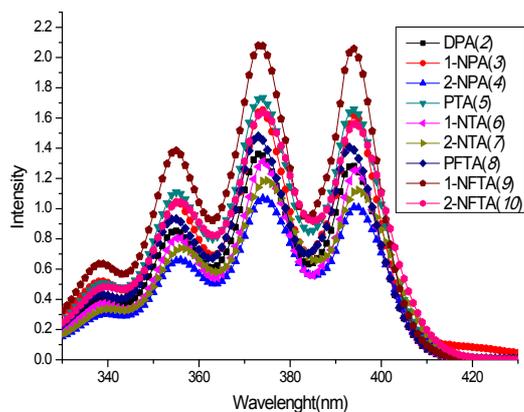


Fig. 1. Absorption spectra of compounds (2~10) in cyclohexane

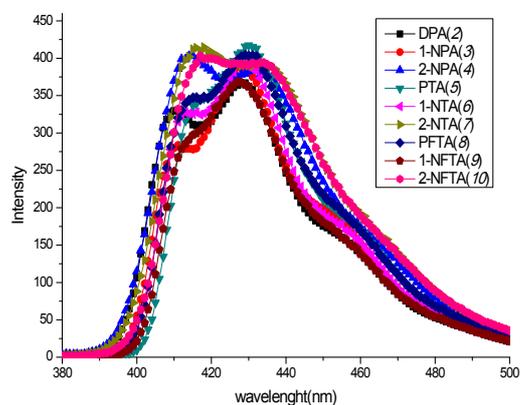


Fig. 2. Emission spectra of compounds (2~10) in cyclohexane.

Molecular orbitals of all the compounds have been checked. They are similar to the other anthracene derivatives [14,15], not co-planar between anthracene and side aryl groups. The aryl substituents contribute little to the orbitals of anthracene. The dihedral angle between anthracene and 2-naphthyl is the largest among them.

Band gap energy (E_g) of compounds have

been calculated from UV-vis spectrum in Fig 1. There seems to show little variation throughout the derivatives.

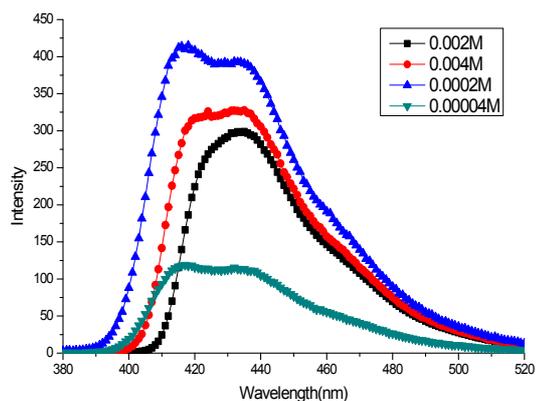


Fig. 3. PL spectra of 2-NTA in different concentrations ($10^{-3} \sim 10^{-5}$ M)

4. Conclusion

Some anthracene derivatives with aryl groups are prepared for the blue emitting materials in OLED. Molecular modeling shows that the HOMO and LUMO of those molecules are mostly focused at the anthracene rather than the substituents. Absorption and emission spectra bands of the compounds are similar to each other, irrelevant to the substituents. The emission bands of solid state as well as of the concentrated solution are red-shifted by about 20nm implying that the excimer is produced. According to preliminary test of OLED, all the compounds in this paper are suitable for device. In particular, 2-NTA (7) is most promising than the others. In conclusion, anthracene derivatives are surely blue emitting regardless to the substituents. Even simple

Table 2. C.I.E. data of anthracene derivatives 2~10.

| substituents | phenyl | 1-naphthyl | 2-naphthyl |
|-----------------------------|------------------|------------------|-------------------|
| phenyl | 2 (0.163, 0.150) | 3 (0.157, 0.130) | 4 (0.156, 0.111) |
| <i>p</i> -tolyl | 5 (0.173, 0.169) | 6 (0.162, 0.146) | 7 (0.158, 0.128) |
| <i>p</i> -(trimethyl)phenyl | 8 (0.167, 0.230) | 9 (0.173, 0.204) | 10 (0.172, 0.185) |

derivatives show deep-blue emission and thermal stability. The electric properties for the OLED application are under investigation.

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