

Synthesis and Electroluminescent Properties of Fluoranthene Derivatives

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Abstract

As a new fluoranthene derivative, a synthesis of benzo[k]fluoranthene was suggested, so new blue emitting materials, 7,12-diphenylbenzo[k]fluoranthene [DPBF] and 7,8,10-triphenylfluoranthene [TPF] were synthesized.

EL_{max} wavelength of the device using DPBF as an emitting layer was 436 and 454nm in the deep-blue region, which are similar values with PL. The device that used DPBF as an emitting layer showed high efficiency of 2.11cd/A and the excellent color coordinate value of (0.161, 0.131) in deep-blue region.

[DPBF] was synthesized. Also, for a relative comparison of synthesized materials, 7,8,10-triphenylfluoranthene [TPF]¹⁰ which was recently reported as an excellent blue emitter was synthesized as well.

Through differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), cyclic voltammetry (CV), and UV-visible and photoluminescence (PL) spectroscopy, thermal, electrical, and optical properties of three synthesized materials were identified. Furthermore, multi-layered EL device was fabricated to identify electroluminescent properties of the materials.

1. Introduction

Different from LCD, organic light-emitting diodes (OLED) developed by C.W. Tang in 1987 is provide self-emission property that does not require backlight. Since it allows to produce light-weight display with thin thickness that can self-emit, it is most appropriate to realize flexible display¹⁻⁵. However, currently available OLED has many issues to be resolved and one of the most critical issues is blue emitting material. For full color display applications, red⁶, green⁷, and blue⁸ emitting materials are needed; only when both efficiency and life-time of red, blue, and green are excellent, it is possible to commercialize full-color devices. Recent studies developed materials with which both red or green have high efficiency of 10cd/A and 100,000 hours of lifetime, but blue emitting materials have not reached these with maximum capacity of 7cd/A and 12,000 hours⁹. Therefore, it is imperative to find new blue emitting materials with long lifetime, and it is necessary to carry out studies on various types of new blue emitting materials.

As a new fluoranthene derivative, a synthesis of benzo[k]fluoranthene was suggested, so a new blue emitting material, 7,12-diphenylbenzo[k] fluoranthene

2. Experimental

2.1. Synthesis

2.1.1. 7,12-diphenylbenzo[k]fluoranthene[DPBF]

Acenaphthylene(1g, 4.93mmol) and 1,3-diphenylisobenzofuran(1.5g, 5.42mmol) were added to Acetic Acid (150 mL), then HBr (1ml) was added into the reaction mixture. The mixture was heated to 100°C for 2 h under nitrogen. After the reaction had finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried with anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered and washed with methanol.

The yellow powder was purified by using column chromatography with CHCl₃ : n-hexane (1:3) eluent to afford a beige solid (DPBF) (yield = 1.8 g, 90.3 %).

¹H NMR (δ ,ppm) : 7.65(m, 10H), 7.57(d, 4H), 7.39(q, 2H), 7.31(t, 2H), 6.61(s, 2H); Fab+-mass: 404.

2.1.2. 7,9-diphenyl-8H-cyclopenta[a]acenaphthylene-8-one

1,3-Diphenyl-2-propanone(1g, 4.7mmol) and acenaphthoquinone(0.8g, 4.4mmol) were added to

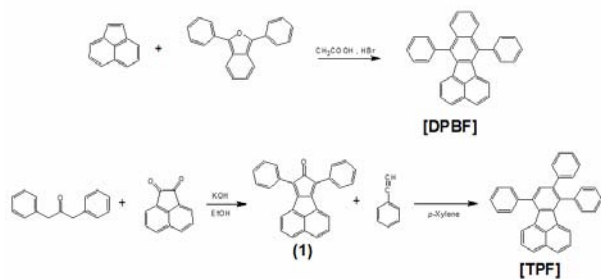
Ethanol (100 mL), then 1M KOH solution(5mL, 5mmol) was added into the reaction mixture. The mixture was heated to 50°C for 3 h under nitrogen. The reactant mixture was cooled after 1 h and then the product was filtered and washed with ethanol. (yield = 1.45g , 92.5%)

$^1\text{H NMR}$ (δ , ppm) : 8.07(d, 2H), 7.87(d, 2H), 7.83(d, 4H), 7.59(t, 2H), 7.52(t, 4H), 7.41(t, 2H) ; Fab^+ -mass : 356.

2.1.3. 7,8,10-triphenylfluoranthene[TPF]

7,9-diphenyl-8H-cyclopenta[a]acenaphthyl-en-8-one (1g, 2.81mmol) and ethynylbenzene (0.4ml, 3.6mmol) were added to xylene (100 mL). The mixture was heated to 130°C for 3h under nitrogen. After the reaction had finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried with anhydrous MgSO_4 and filtered. The solution was evaporated. The residue was dissolved in CHCl_3 and added to methanol. The precipitate was filtered and washed with methanol. The yellow powder was purified by using column chromatography with CHCl_3 : n-hexane (1:3) eluent to afford a yellowish-beige solid (TPF) (yield = 1.05 g, 86.9 %).

$^1\text{H NMR}$ (δ , ppm) : 7.72(m, 4H), 7.55(t, 2H), 7.52(t, 1H), 7.36(m, 6H), 7.33(s, 1H), 7.30(t, 2H), 7.23(d, 2H), 7.17(m, 3H), 6.68(d, 1H) ; Fab^+ -mass : 430.



Scheme 1. Synthetic routes of synthesized materials.

2.2. General methods

$^1\text{H-NMR}$ spectra were recorded on a Bruker, Advance DPX-300. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were measured by a HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50(Xenon flash tube) was used for photo- and electro-luminescence spectroscopy. The melting temperatures (T_m), glass-transition temperatures (T_g) and degradation temperatures (T_d) of the compounds were measured by carrying out

differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC2910 (TA Instruments) and thermogravimetric analysis (TGA) using a SDP-TGA2960 (TA Instruments). Redox potential of the compounds were determined by cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of 150mV/s. The synthesized compounds were dissolved in N,N-Dimethylformamide (DMF) with 0.1M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and a saturated Ag/AgNO_3 reference electrode. Ferrocene was used for potential calibration (all reported potentials are reference against ferrocene/ferrocenium, FOC) and for reversibility criteria.

For the EL devices, all organic layers were deposited under 10^{-6} torr, with a rate of deposition of $1 \text{ \AA}/\text{s}$ to give an emitting area of 4 mm^2 . The LiF and aluminum layers were continuously deposited under the same vacuum conditions.

The current-voltage (I-V) characteristics the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-100A.

3. Results and discussion

Synthetic routes of two fluoranthene derivatives are described in Scheme 1.

After synthesis of 7,9-diphenyl-8H-cyclopenta[a]acenaphthyl-en-8-one(compound 1) (yield = 90%) by using Knoevenagel condensation, it was again synthesized with ethynylbenzene through Diels-Alder reaction to get TPF. 7,12-diphenylbenzo[k]fluoranthene [DPBF] also synthesized with acenaphthylene and 1,3-diphenylisobenzofuran through Diels- Alder reaction. All steps showed high yield of more than 80%.

Synthesized materials were vacuum-deposited on glass to measure UV-visible and PL spectrum and the measured values of UV-visible and PL spectrum are shown in Table 1. Figure 1 and 2 shows UV-Visible and PL spectra of TPF and DPBF films.

	UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	FWHM	HOMO	LUMO	E_g (eV)
TPF	410	381	458	78	5.84	2.82	3.02
DPBF	426	415	434,453	45	5.70	2.79	2.91

Table 1. Optical and electrical properties of synthetic compounds.

According to UV data in Figures 1 and 2, TPF and DPBF show different UV_{max} values of 381nm and 415nm, respectively. The structure of synthesized molecules shows that DPBF with benzo[k]fluoranthene has a relatively longer conjugation length than TPF with fluoranthene, which makes UV_{max} longer.

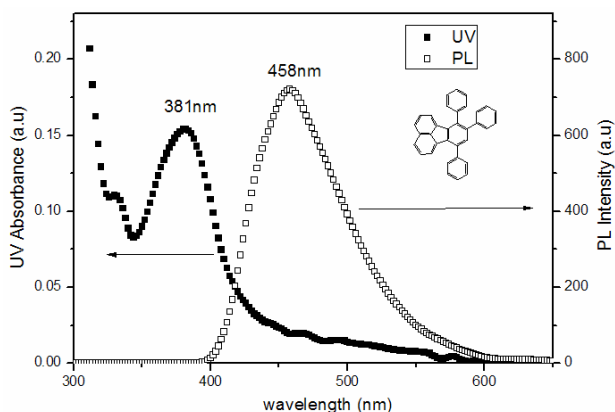


Figure 1. UV-visible(solid) and PL Spectrum(open) of TPF film on glass.

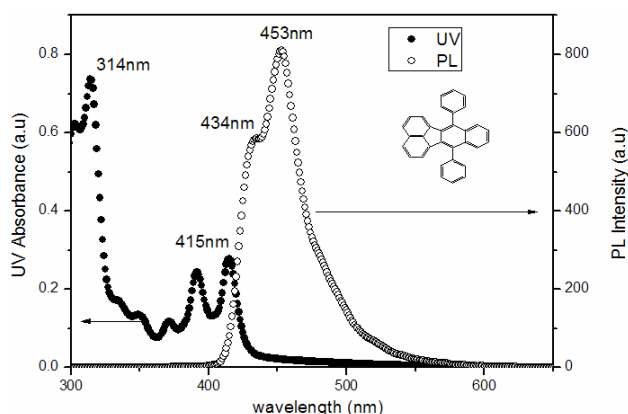


Figure 2. UV-visible(solid) and PL Spectrum(open) of DPBF film on glass.

PL_{max} values of both compounds showed 458nm (TPF) and 434nm, 453nm (DPBF) wavelength, which are blue emission. Based on the results of FWHM in PL, DPBF with 45nm has a sharper shape than TPF with 78nm, which indicates that DPBF has a relatively simpler state of transition than TPF. According to a molecular structure, TPF has an asymmetrical structure that enables three phenyls to rotate. On the contrary, DPBF has a symmetrical structure, and only two phenyls can rotate. Therefore, DPBF has a relatively small number of transitions in a molecule narrowing PL spectrum. As a result, PL peak value in the 434nm area of TPF is included into a broad range of PL peak without being distinguished. However,

PL_{max} values of the two materials were found to be similarly close to 455nm. Based on these results, it is possible to assume that fluoranthene can act as a major part determining PL_{max} value and that the substituted phenyl groups decide the width of PL wavelength.

CV was measured to identify HOMO values of synthesized materials. Even when cycles are scanned for more than 50 times or so, CV result appeared stable.

By using band-gap identified with UV_{onset} and HOMO value measured through CV, LUMO level was confirmed, and they are summarized in Table 1. The HOMO levels of both compounds were lower than NPB (5.4eV) which is a hole transporting material; the LUMO levels were higher than Alq₃ (3.1eV) which is electron transporting material, showing an adequate electronic level as an emitting layer. The HOMO level of DPBF was found to be a little higher than that of TPF, while the LUMO level of DPBF is slightly lower than that of TPF. This is attributed to the process in which the increased conjugation of DPBF increases HOMO but decreases band gap.

Multi-layered OLED device was fabricated in order to identify electroluminescent properties of synthesized materials. Device configuration is as follows: ITO/2-TNATA (60 nm)/NPB (15 nm)/TPF or DPBF (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (200 nm). For an objective comparison of electroluminescent properties of DPBF, reference device using DPVBi was fabricated: ITO/2-TNATA (60 nm)/NPB (15 nm)/DPVBi (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (200 nm).

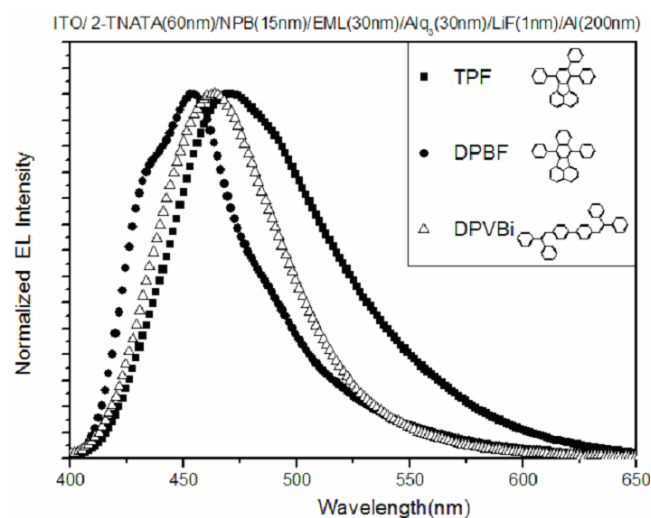


Figure 4. EL Spectrum of ITO/2-TNATA/NPB/TPF(■), DPBF(●) and DPVBi(△) /Alq₃ /LiF/Al devices at 10 mA/cm².

Figure 4 illustrates EL spectra of the fabricated devices. EL_{max} wavelength of the device that used DPBF as an emitting layer shows very similar values 436 and 454nm with PL which is a deep-blue region. The device that used DPVBi and TPF as an emitting layer had 464, 471nm of EL_{max} which is more red-shifted than the device with DPBF. In terms of the shape of EL spectrum, like that of PL spectrum, DPBF was most narrow.

	EL _{max} (nm)	Voltage (V)	Luminance Efficiency (cd/A)	Power Efficiency (lm/W)	CIE (x,y)
TPF	471	6.3	3.27	1.63	(0.192, 0.269)
DPBF	436, 454	6.1	2.11	1.09	(0.161, 0.131)
DPVBi	464	8.2	3.12	1.20	(0.151, 0.155)

Table 2. EL performance of multi-layered devices with the structure: ITO /2-TNATA(60 nm) /NPB(15 nm) /TPF or DPBF or DPVBi(30 nm) /Alq₃(30 nm) /LiF(1 nm) /Al(200 nm) at 10 mA/cm².

Table 2 shows efficiency of the fabricated device at 10mA/cm² of current density. The device using TPF as an emitting layer showed the highest efficiency of 3.27cd/A, but the greenish-blue color coordinate value of (0.192, 0.269) was shown due to the effect of wide EL spectrum. The device using DPVBi showed the Commission International d'Eclairage (CIE) coordinate value of (0.151, 0.155) in blue region.

While the device that used DPBF as an emitting layer had a relatively low efficiency of 2.11cd/A, it had low turn-on voltage and excellent color coordinate value of (0.161, 0.131) in very deep-blue region. The characteristics of blue materials are very much reliant on the values on the Y-axis of CIE and it is very difficult to obtain the values of 0.15 and lower in Y axis. In other words, it is confidently suggested that the property of blue color coordinate value of DPBF is superior to commercialized blue material, DPVBi. When these excellent color coordinate property of DPBF is applied to the host-dopant system, it is possible to fabricate OLED blue device with high performance.

4. Summary

As a novel fluoranthene derivative, benzo[k]fluoranthene was synthesized and presented to synthesize a novel blue emitting material, 7,12-diphenylbenzo[k] fluoranthene[DPBF]. PL_{max} values of both compounds showed the wavelengths of 458nm (TPF) and 434nm, 453nm (DPBF) that are in blue region.

EL_{max} wavelength of the device using DPBF as an emitting layer was 436 and 454nm in the deep-blue region, which are similar values with PL. The device that used DPBF as an emitting layer showed high efficiency of 2.11cd/A and the excellent color coordinate value of (0.161, 0.131) in deep-blue region.

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