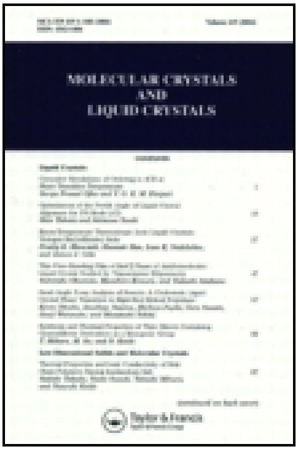

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New Fluoranthene Derivatives in Electroluminescence

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New Fluoranthene Derivatives in Electroluminescence

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7,8,10-triphenylfluoranthene [TPF], 7,10-diphenyl-8-(1-naphthyl) fluoranthene [DPNF], 7,10-diphenyl-8-(9-phenanthrenyl)fluoranthene[DPPF] were synthesized by using the Knoevenagel condensation and Diels–Alder addition. PL maximum values of TPF, DPNF and DPPF are 458 nm, 460 nm and 461 nm, respectively. TPF showed sky-blue CIE value of (0.192, 0.269) and 3.27cd/A at 10 mA/cm^2. DPNF also showed sky-blue CIE value of (0.189, 0.262) and 3.24 cd/A at 10 mA/cm^2. DPPF showed much better operating voltage, luminance and power efficiency of 3.96 cd/A and 2.11 lm/W although it had worse C.I.E. value than TPF.

Keywords: blue emitting material; Diels–Alder addition; fluoranthene; OLED; spartan

INTRODUCTION

If Organic light-emitting diodes (OLEDs) based on organic molecules are currently the intensive subject due to their promise for full-color large display applications [1–5].

Recent studies developed materials with which both red or green have high efficiency of 10 cd/A and 100,000 hours of lifetime, but blue emitting materials have not reached these with maximum capacity of 7 cd/A and 12,000 hours [6].That blue material having relatively low

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efficiency and short device life-time is attributed to the fact that more than 3.0 eV of band-gap is needed to have blue light. Compared to red or green emitting materials, band-gap is relatively wide, increasing energy gap between layers, which causes charge-balance to mismatch between hole and electron. As a result, low luminance efficiency and high operating voltage are found, which leads material degradation by heating and further reduction of lifetime. Of the materials that have reported as blue materials such as Diarylanthracene [7], di(styryl) arylene [8] and pyrene [9], 4,4′-bis(2,2-diphenylvinyl)-1,1′-biphenyl (DPVBi) [8] is considered most representative. However, DPVBi has the lowest value of Tg, 64°C [10] and it is well known that low Tg has a considerable influence on life-time. 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.

In this study, we synthesized 7,8,10-triphenylfluoranthene [TPF] [11] and TPF derivatives which are substituted by 1-naphthyl and 9-phenanthrenyl instead of phenyl at 8- position.

The materials 7,8,10-triphenylfluoranthene [TPF], 7,10-diphenyl-8-(1-naphthyl) fluoranthene [DPNF], 7,10-diphenyl-8-(9-phenanthrenyl) fluoranthene [DPPF] were synthesized by using the Knoevenagel condensation and Diels–Alder addition.

The thermal and electro-optical properties of these materials were characterized with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), cyclic voltammetry (CV), and UV-visible and photoluminescence (PL) spectroscopy. Moreover, multilayered EL devices were fabricated using these materials as non-doped emitting layers.

EXPERIMENTAL

Synthesis

7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one(1)

1,3-Diphenyl-2-propanone (10 g, 47 mmol) and acenaphthoquinone (8 g, 44 mmol) were added to Ethanol (300 mL), then 1 M KOH solution (47 mL, 47 mmol) 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 = 14.5 g, 92.5%)

^{1}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

7,8,10-triphenylfluoranthene[TPF]

7,9-diphenyl-8H-cyclopenta[a]acenaphthylen-8-one (2 g, 5.62 mmol) and ethynylbenzene (0.7 ml, 6.3 mmol) were added to xylene (200 mL). The mixture was heated to 130°C for 10 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 $MgSO_4$ 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 = 2.1 g, 86.9%).

^{1}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

7,10-diphenyl-8-(1-naphthyl)fluoranthene [DPNF] and 7, 10-diphenyl-8-(9-phenanthrenyl) fluoranthene [DPPF]

DPNF and DPPF were synthesized as for the above series by using Diels-Alder addition.

[DPNF] (yield = 90%) ^{1}H NMR (δ, ppm) : 7.85 (d, 1H), 7.77 (d, 2H), 7.73 (d, 3H), 7.66 (d, 1H), 7.53 (t, 2H), 7.49 (d, 1H), 7.44 (d, 1H), 7.39 (m, 4H), 7.31 (m, 5H), 7.16 (t, 1H), 7.08 (d, 1H), 7.05 (t, 1H), 6.66 (d, 1H); Fab$^+$-mass : 480

[DPPF] (yield = 83%) ^{1}H NMR (δ, ppm) : 8.62 (t, 2H), 7.90 (d, 1H), 7.75 (m, 5H), 7.59 (t, 3H), 7.50 (m, 6H), 7.40 (q, 2H), 7.35 (s, 1H), 7.28 (t, 1H), 7.18 (m, 2H), 7.10 (t, 1H), 7.04 (t, 1H), 6.63 (d, 1H); Fab$^+$-mass : 530

Characterization

^{1}H NMR spectra were recorded on Bruker Avance 500 spectrometers. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. The optical absorption spectra were obtained with a HP 8453 UV-VIS-NIR spectrometer. 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). A Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo- and electro-luminescence spectroscopy. The redox potentials of the compounds were determined with cyclic voltammetry

(CV) using an EG&G 362 electrochemical workstation with a scanning rate of 50 ~ 200 mV/s. The synthesized materials were dissolved in N,N-dimethylformamide (DMF) with 0.1 M 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 and for reversibility criteria.

Density functional theoretical calculations were performed using Spartan'04 (for Windows) [12]. The structures were drawn at the entry-level of input and minimized. Equilibrium geometry was obtained at the B3LYP level of DFT for each molecule at the ground state from its initial geometry subject to symmetry with a 6-31G* basis set [13]. Orbitals and energies, atomic charges, vibrational modes, and thermodynamic properties were chosen as output parameters. HOMO and LUMO orbital surfaces were then obtained from the output.

For the EL devices, all organic layers were deposited under 10^{-6} torr, with a rate of deposition of 1 Å/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 of the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-100A.

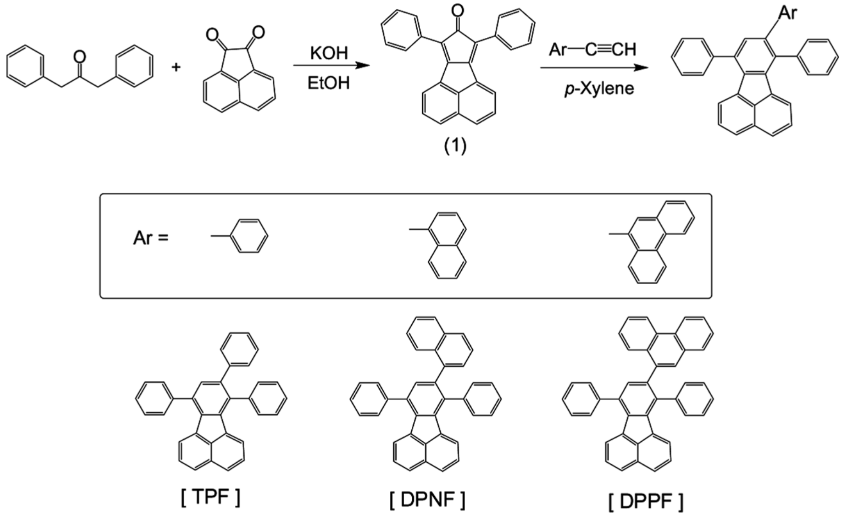
RESULTS AND DISCUSSION

Synthetic routes of three fluoranthene derivatives are described in Scheme 1. All compounds were obtained by using the Knoevenagel condensation and Diels-Alder addition.

All steps showed high yield of more than 80%. Especially it was possible to synthesize the final compound without using metal complex catalyst. This is intended to exclude a possibility that even a very small amount of metal complex could exist in the final compound. It is not easy to remove small residue portion of metal complex in synthesized compounds with various purification methods as well as sublimation. Therefore, it is possible to expect high purity of the materials and the improved life-time of device in case of this synthesis scheme.

In the last step of purification, recrystallization and silica column were performed for all synthesized materials to increase their purity, and structures were identified with NMR and Fab-Mass analysis.

Synthesized materials are placed on glass to make a film through vacuum deposition, and UV-Visible and PL spectra are measured. The data are summarized in Table 1.



SCHEME 1 Synthetic routes of TPF, DPNF and DPPF.

The maximum absorbance of TPF, DPNF and DPPF appeared at around 381, 380 and 380 nm, respectively. PL_{max} values of three compounds showed 458 nm (TPF), 460 nm (DPNF) and 461 nm (DPPF) wavelength, which are blue colors. Moreover, in terms of FWHM values, TPF has the sharpest peak with 79 nm, and as the 8-position's aromatic ring number increased, FWHM value also increased. This is attributed to the inference that when molecular structure became more complex, the types of transition within molecule increased. However, UV_{max} and PL_{max} values of the three materials were found to be similarly close to 380 nm and 460 nm. Based on these results, it is possible to assume that fluoranthene provides a major optical property that determines UV_{max} and PL_{max}.

The ground-state structures and electron state of HOMO and LUMO were calculated using by B3LYP/6-31G* method of Spartan'04 program [12,13].

TABLE 1 Optical, Electrical and Thermal Properties of Synthetic Compounds

	UV_{onset} (nm)	UV_{max} (nm)	PL_{max} (nm)	FWHM (nm)	HOMO (eV)	LUMO (eV)	Eg (eV)	T_g (°C)	T_m (°C)	T_d (°C)
TPF	410	381	458	79	5.84	2.82	3.02	–	199	323
DPNF	409	380	460	81	5.88	2.85	3.03	106	228	347
DPPF	412	380	461	85	5.88	2.87	3.01	136	303	371

TABLE 2 Comparison of Distances and Dihedral Angles in Fluoranthene Derivatives at the Ground State (at Spartan'04/B3LYP/6-31G*)

	7		8		10	
Position @ fluoranthene	Distance (Å)	Dihedral (deg)	Distance (Å)	Dihedral (deg)	Distance (Å)	Dihedral (deg)
TPF	1.496	71.91	1.493	55.10	1.492	58.20
DPNF	1.496	72.40	1.498	72.13	1.491	57.04
DPPF	1.496	75.56	1.499	77.07	1.491	56.98

When the ground-state structures of three molecules were examined, it was found that the distance between fluoranthene and 7-, 8-, 10- phenyl groups in TPF was almost identical. When bulky groups were introduced into 8-position, it caused twisted chemical structures and different dihedral angles as shown in Table 2.

Figure 2 shows HOMO and LUMO electron distribution of TPF, DPNF and DPPF. According to Figure 2, electron density of HOMO and LUMO in TPF, DPNF, and DPPF spreads overall on fluoranthene moiety. HOMO electrons of DPNF and DPPF was also located at 8-position, which might be due to slight electron-withdrawing effect.

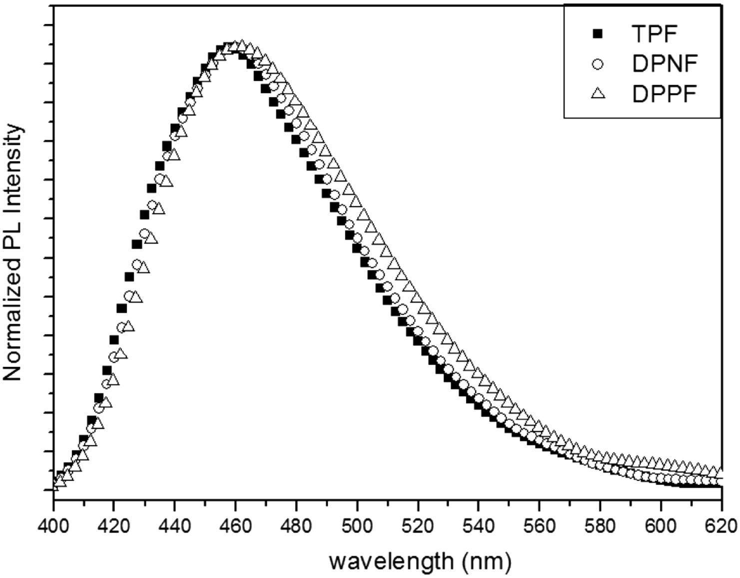


FIGURE 1 Normalized PL Spectra of TPF(■), DPNF(○) and DPPF(△) film on glass.

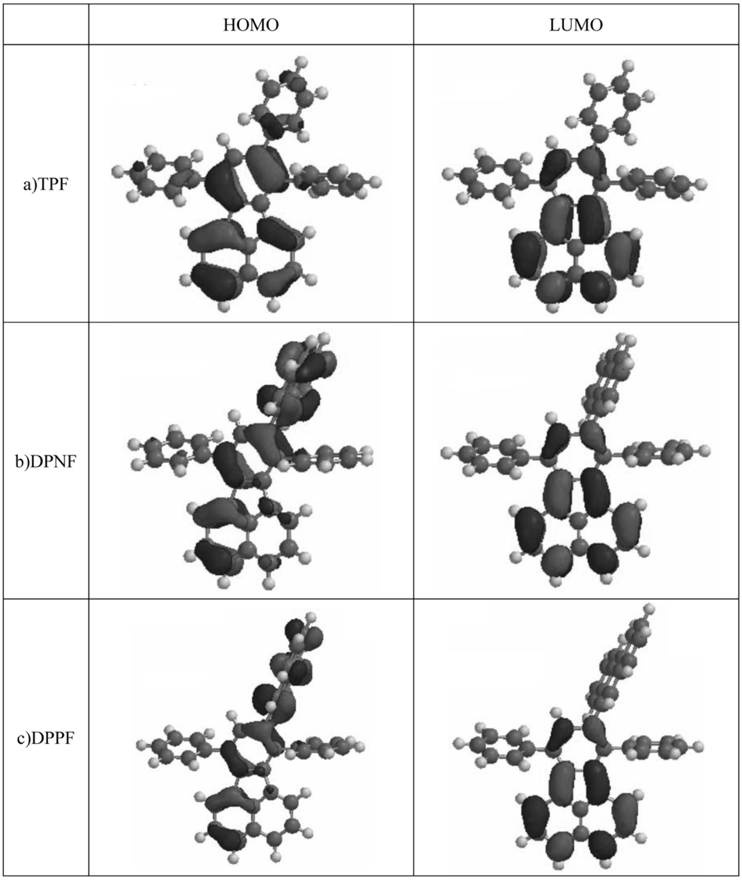


FIGURE 2 HOMO and LUMO levels of (a) TPF, (b) DPNF and (c) DPPF calculated at the B3LYP/6-31G* level of density functional theory with a 6-31G* basis set using Spartan'04.

HOMO and LUMO levels, which determine band gap in all compounds, confirmed that electron density is concentrated on. HOMO and LUMO results explain why UV_{max} and PL_{max} values of three compounds are similar.

CV was measured to identify HOMO values of the 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 values measured through CV, LUMO was confirmed, which are summarized in Table 1. The HOMO levels of three materials showed very similar values in the range of $5.8 \sim 5.9$ eV. That is, it is expected that oxidation and reduction within molecules occur in fluoranthene regardless of substituents. This result can be associated with the finding obtained through molecular simulation that the most of electrons on HOMO and LUMO exist in fluoranthene. The HOMO levels of both compounds were lower than NPB (5.4 eV) which is a hole transporting material; the LUMO levels were higher than Alq3 (3.1 eV) which is electron transporting material, showing an adequate electronic level as emitting layer.

TGA and DSC data analysis identified important thermal properties of the synthesized materials which is directly related to the life-time property of device as mentioned above (Table 1). TGA data under the condition of nitrogen showed T_d of the materials as shown in Table 1. Temperatures at which the weight is reduced by 5% were 323°C (TPF), 347°C (DPNF) and 371°C (DPPF). Through DSC, it were found that TPF, DPNF and DPPF had T_m values of 199°C, 228°C and 303°C. T_g of TPF was not detected and T_g of DPNF and DPPF exhibited 106°C and 136°C. Considering that T_g and T_m of DPVBi is 64°C [10] and 204°C [14], thermal properties of these materials are assumed to be excellent.

Multi-layered OLED device was fabricated in order to identify electroluminescent properties of synthesized materials. OLED device structures are as follows: ITO/2-TNATA (60 nm)/NPB (15 nm)/TPF or DPNF or DPPF (30 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (200 nm).

Figure 3 shows the I-V curves of the devices. The synthesized materials showed similar I-V characteristics, which is due to similar HOMO and LUMO levels.

Figure 4 illustrates EL spectrum of the fabricated device. The device that used TPF, DPNF and DPPF as emitting layers shows EL_{max} values of 471 nm, 470 nm and 478 nm, respectively, in the sky-blue area.

Table 3 shows efficiency and CIE values of the fabricated devices at 10 mA/cm^2 of current density. TPF showed sky-blue CIE value of (0.192, 0.269) and 3.27cd/A at 10 mA/cm^2. DPNF also showed sky-blue CIE value of (0.189, 0.262) and 3.24 cd/A at 10 mA/cm^2. DPPF showed much better operating voltage, luminance and power efficiency of 3.96 cd/A and 2.11 lm/W. DPNF including a Naphthyl group at 8-position exhibited similar EL efficiency and CIE values, but DPPF having a Phenanthrenyl group showed better luminance and power efficiency than TPF. We believe that side-group moiety can change the EL efficiency of fluoroanthene derivatives. We also think that in order to increase red EL efficiency, Phenanthrene could be good candidate for side group.

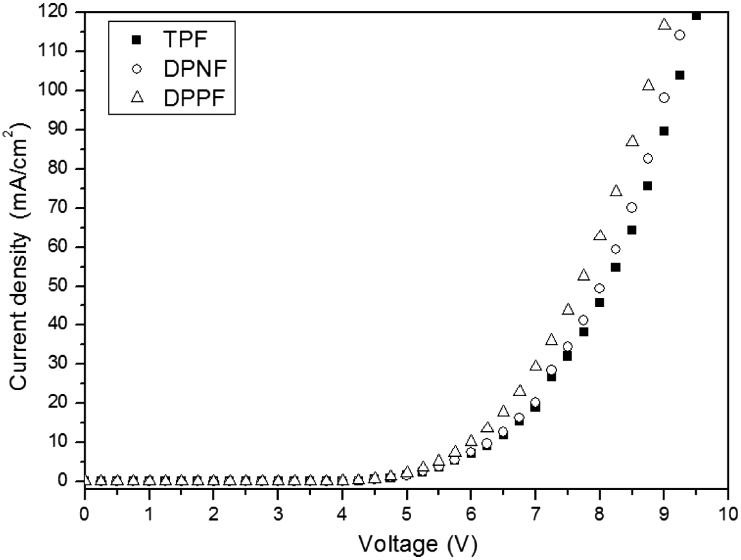


FIGURE 3 Current density-voltage characteristics of ITO/2-TNATA(60 nm)/NPB(15 nm)/TPF(■), DPNF(○) and DPPF(△)(30 nm)/Alq_3(30 nm)/LiF(1 nm)/Al devices.

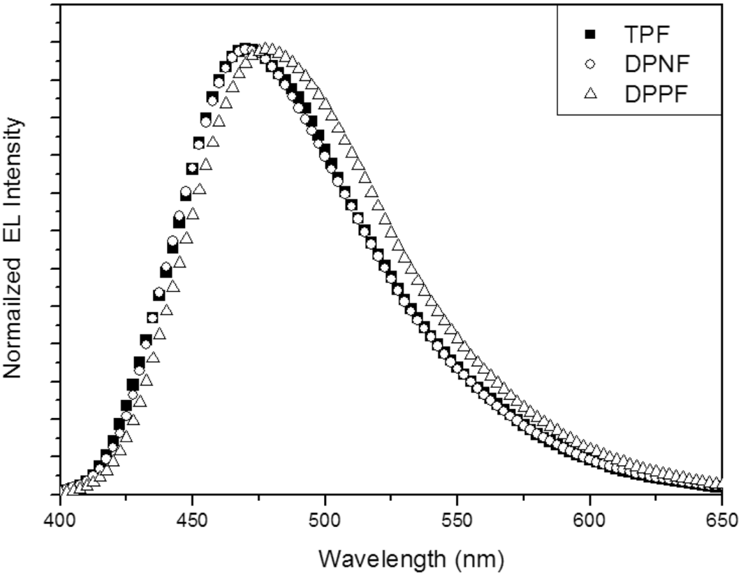


FIGURE 4 EL Spectrum of ITO/2-TNATA/NPB/TPF(■), DPNF(○) and DPPF(△)/Alq_3/LiF/Al devices at 10 mA/cm^2.

TABLE 3 EL Performance of Multi-Layered Devices with the Structure: ITO/2-TNATA(60 nm)/NPB(15 nm)/Synthesized Material(30 nm)/Alq_3(30 nm)/LiF (1 nm)/Al(200 nm) at 10 mA/cm^2

	EL_{max} (nm)	Voltage (V)	Efficiency (cd/A)	Efficiency (lm/W)	CIE (x, y)
TPF	471	6.3	3.27	1.63	(0.192, 0.269)
DPNF	470	6.2	3.24	1.64	(0.189, 0.262)
DPPF	478	5.9	3.96	2.11	(0.217, 0.326)

CONCLUSIONS

7,8,10-triphenylfluoranthene [TPF], 7,10-diphenyl-8-(1-naphthyl) fluoranthene [DPNF], 7,10-diphenyl-8-(9-phenanthrenyl)fluoranthene [DPPF] were synthesized by using the Knoevenagel condensation and Diels-Alder addition. The maximum absorbance of TPF, DPNF and DPPF appeared at around 381, 380 and 380 nm, respectively. PL_{max} values of three compounds showed 458 nm (TPF), 460 nm (DPNF) and 461 nm (DPPF) wavelength, which are blue colors. TPF showed sky-blue CIE value of (0.192, 0.269) and 3.27 cd/A at 10 mA/cm^2. DPNF also showed sky-blue CIE value of (0.189, 0.262) and 3.24 cd/A A at 10 mA/cm^2. DPPF showed much better operating voltage, luminance and power efficiency of 3.96 cd/A and 2.11 lm/W. DPNF including a Naphthyl group at 8-position exhibited similar EL efficiency and CIE values, but DPPF having a Phenanthrenyl group showed better luminance and power efficiency than TPF.

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