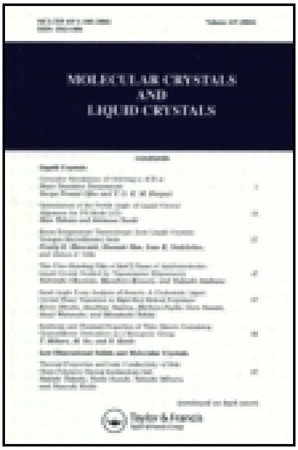

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Synthesis of Dopant with Phenothiazine Moiety and Polymer Electroluminescence Device Properties

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SYNTHESIS OF DOPANT WITH PHENOTHIAZINE MOIETY AND POLYMER ELECTROLUMINESCENCE DEVICE PROPERTIES

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(N-2-ethylhexyl)-3(6)-phenothiazinylene vinylene-co-9,10-anthrylene vinylene), KPD-1, as a new low molecular weight dopant was synthesized. Poly(1,12-dodecanedioxy-2-methoxy-1,4-phenylene-1,2-ethenylene-1,1′-biphenyl-4,4′-ylene-1,2-ethenylene-3-methoxy-1,4-phenylene), [Poly(BFMP$_{12}$*-AV)], as a matrix polymer was also prepared by Honer-Emmons condensation. Single- and multi-layered PLEDs were fabricated with a mixture of dopant/matrix polymer as an emissive layer. The effect of dopant/matrix polymer and device structures on the energy transfer and electro-optical properties of doped PLEDs was discussed in terms of emission color changes and luminescence efficiency of doped PLEDs.*

Keywords: conjugated polymer; dopant/matrix system; energy transfer; Horner-Emmons condensation; light-emitting diode

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INTRODUCTION

Research into conjugated polymers have been motivated by their promising application in light-emitting diodes (LEDs), since R. H. Friend *et al.* reported LED made from poly(*p*-phenylenevinylene) [1,2]. It has been generally accepted [3,4] that the electrochemical structure and nanostructures of conjugated polymers has played a key role on the electro-optical properties of LEDs. However, a few of conjugated polymers have been satisfied with the required performance. It has been reported that electroluminescent properties in PLEDs are improved either by contructing multi-layer devices or by incorporating low molecular weight dopant in the emissive layer. Therefore, the use of proper dopant with high color purity and energy transfer capability could be one approach to improve electro-optical properties of PLEDs.

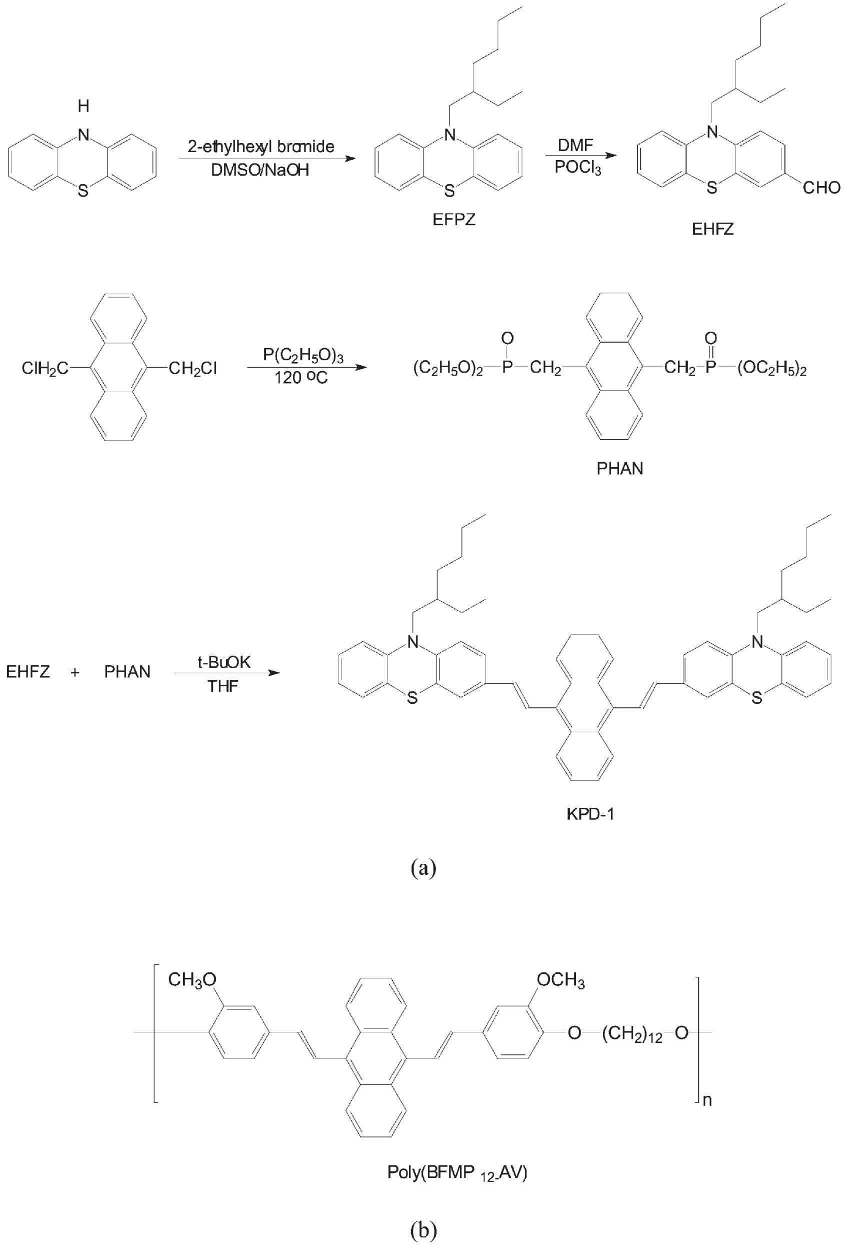
In this work we synthesized a new low molecular weight dopant with both phenothiazine and anthracene moieties which had similar structure with poly(BFMP$_{12}$-AV) matrix polymer reported by our laboratory [5]. Single- and double-layered PLEDs were fabricated with polymeric matrix/dopant layer as an emissive layer and evaluated in terms of emission color and luminescence efficiency.

EXPERIMENTAL

Synthesis

Synthesis of (*N*-2-ethylhexyl)-3(6)-phenothiazinylene vinylene-*co*-9,10-anthrylene vinylene) (KPD-1). Firstly *N*-(2-ethylhexyl)phenothiazine (EHPZ) was synthesized from the reaction of phenothiazine (6 g, 0.03 mol) and 2-ethylhexylbromide (5.8 g, 0.03 mol) in the presence of sodium hydroxide (7.2 g, 0.18 mol) in dimethylsulfoxide (60 ml) at room temperature for 3 h [11]. Yield: 73%. ^{1}H NMR(CDCl$_3$), δ: 6.87, 7.12 (m, 8H, Ar-$\boldsymbol{H}$), 3.70 (m, 2H, N-C$\boldsymbol{H}_2$–), 1.93 (t, 1H, C$\boldsymbol{H}$–), 1.22–1.44 (m, 9H, –C$\boldsymbol{H}_2$–), 0.83–0.87 (m, 6H, –C$\boldsymbol{H}_3$), IR (KBr), cm^{-1}: 3064 (Ar CH), 2926 (aliphatic CH), 2857 (N–CH$_2$–), 1593, 1485 (Ar C=C).

N-(2-Ethylhexyl)-3(6)-formylphenothiazine (EHFZ) was synthesized using modified Vilsmeier-Haack formylation in the second step [6,7]. Yield : 45%, ^{1}H NMR(CDCl$_3$), δ: 9.73 (m, 2H, aldehydic hydrogen), 6.88, 7.56 (m, 6H, Ar $\boldsymbol{H}$), 3.73 (t, 2H, N–C$\boldsymbol{H}_2$–), 1.17–1.85 (m, 9H, –C$\boldsymbol{H}_2$–, C$\boldsymbol{H}$–), 0.76–0.82 (m, 6H, –C$\boldsymbol{H}_3$), IR (KBr), cm^{-1}: 3048 (Ar CH; weak signal), 2927 (aliphatic CH), 2857 (N–CH$_2$–), 2724 (aldehydic hydrogen), 1688 (C=O), 1600, 1465 (Ar C=C).


H
N
S
2-ethylhexyl bromide
DMSO/NaOH
EFPZ
DMF
POCl3
CHO
EHFZ
ClH2C
CH2Cl
P(C2H5O)3
120 °C
(C2H5O)2
P
O
CH2
(OC2H5)2
PHAN
EHFZ + PHAN
t-BuOK
THF
KPD-1
(a)
CH3O
OCH3
O
(CH2)12
n
Poly(BFMP 12-AV)
(b)

SCHEME 1

9,10-(Chloromethyl)anthracene (4.8 g, 0.014 mol) was reacted with triethylphosphite (30 g, 0.18 mol) at 120°C for 12 h. The unreacted triethylphosphite was removed under reduced pressure [12]. 9,10-Bis(diethoxyphosphinylmethyl)antrhracene (PHAN) was obtained as yellow crystal. Yield: 92%. ^{1}H NMR ($CDCl_3$), δ: 7.57, 8.38 (m, 8H, Ar ***H***), 4.23 (d, 8H, –C***H***$_2$O–P–), 3.84 (m, 4H, Ar–C***H***$_2$–P), 1.06 (t, 12H, –C***H***$_3$), IR (KBr), cm^{-1}: 3026 (Ar CH), 2983 (aliphatic CH), 1251 (P=O).

As presented in Scheme 1(a), KPD-1 was synthesized with adding potassium *tert*-butoxide (4.73 g, 0.04 mol) solution into a mixture of EHFZ (1.70 g, 0.005 mol) and PHAN (1.20 g, 0.0025 mol) in THF, and then stirring at room temperature for 7 h. Yield: 51%, ^{1}H NMR ($CDCl_3$), δ: 6.94 (m, 4H,=C***H***–), IR (KBr), cm^{-1}: 3021 (Ar CH), 2924 (aliphatic CH), 2855 (N–CH_2–), 1578, 1471 (Ar C=C), 965 (trans vinylene).

Poly(BFMP$_{12}$-AV) alternating copolymer, as shown in Scheme 1(b), was obtained by Horner-Emmons condensation reaction [5,8,9].

Fabrication of PLED

The emissive layer (EML) was formed on ITO glass by spin coating of mixture solution of KPD-1 dopant and poly(BFMP$_{12}$-AV) in trichloroethylene. AL electrode (2000 Å thickness) was vacuum deposited by electron-beam method using thermal evaporator (2.0×10^{-5} torr, KVT-420, Korea Vacuum Co.). For multi-layered PLED, PEDOT as a hole transporting layer (HTL) was spin coated to give a thickness of 500 Å or Alq_3 as an electron transporting layer (ETL) was vacuum deposited to a thickness of 300 Å.

Measurements

^{1}H-NMR and FT-IR spectra of synthesized compounds were taken on a Varian Unity Plus 300 and Jasco FT/IR-620 spectrometer, respectively. UV-visible absorption spectra were obtained from Shimadzu UV-2100. Photoluminescence (PL) spectra were obtained by optical multichannel analyzer (OMA system, Lazer Photonics). Excitation source was He-Cd laser (325 nm). Electroluminescence (EL) spectra and color coordinates were measured by using Spectroscan PR 704 (Photoresearch Inc.). Current and luminance vs. voltage profiles were obtained by using a dc power supply connected with model 8092A digital multimeter (Hyun Chang Product Co. Ltd) and luminance meter (Minolta LS-100), respectively.

RESULTS AND DISCUSSION

UV-Vis absorption maximum ($\lambda_{max,UV}$) and PL maximum ($\lambda_{max,PL}$) of poly(BFMP$_{12}$-AV) were measured to be at 299 nm and 338 nm, respectively, as shown in Figure 1. KPD-1 exhibited $\lambda_{\mathrm{max,UV}}$ at 322 nm, which was overlapped to a relatively large extent with PL peaks of poly(BFMP$_{12}$-AV). KPD-1 showed $\lambda_{\mathrm{max,PL}}$ at 374 nm, when excited at its $\lambda_{\mathrm{max,UV}}$. UV-Vis and PL spectra of poly(BFMP$_{12}$-AV)/KPD-1 mixtures were measured as a function of the KPD-1 content in mixtures, as shown in Table 1. It was observed that while $\lambda_{\mathrm{max,UV}}$ values of poly(BFMP$_{12}$-AV)/KPD-1 mixtures remained unchaged, $\lambda_{\mathrm{max,PL}}$ of the mixtures clearly were measured to be in the range of 564–586 nm, higher than $\lambda_{\mathrm{max,PL}}$ of KPD-1 itself. Of the mixtures used, the composition of poly(BFMP$_{12}$-AV)/KPD-1 (97/3 wt./wt.) exhibited the highest $\lambda_{\mathrm{max,PL}}$ among them. It has been well known that the emission by exciplex formation is observed in longer wavelength than normal emission peak [10,11]. Therefore, large shift of PL emission by poly(BFMP$_{12}$-AV)/KPD-1 may be due to the enhanced exciplex formation between the matrix polymer and the dopant at this composition (3 wt.% of KPD-1).

Luminescence vs. voltage profiles of PLEDs such as single-layered ITO/[poly(BFMP$_{12}$-AV)/KPD-1]/Al (S-2 EL device), and double-layered ITO/PEDOT/[poly(BFMP$_{12}$-AV)/KPD-1]/Al (D-1 EL device), ITO/[poly (BFMP$_{12}$-AV)/KPD-1]/Alq$_3$/Al (D-2 EL device) were shown in Figure 2. ITO/[poly(BFMP$_{12}$-AV)/KPD-1]/Alq$_3$/Al (D-2 EL device) had a maximum luminance of 89 cd/m^2 (16 V) and a maximum luminance efficiency of

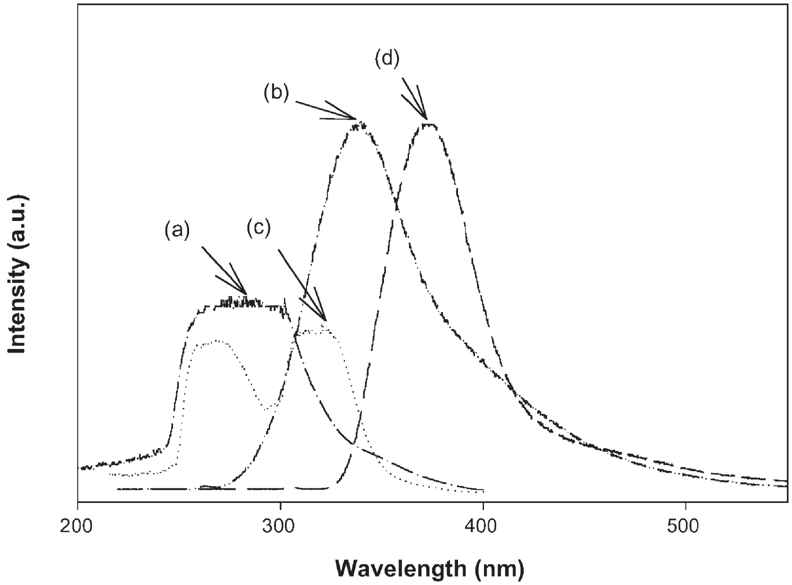


FIGURE 1 UV-Vis and PL spectra in THF; (a) UV-Vis and (b) PL of Poly(BFMP$_{12}$-AV), (c) UV-Vis and (d) PL of KPD-1.

TABLE 1 Electro-optic Data of Matrix/Dopant System

Sample	$\lambda_{\text{max,UV}}$ (nm/eV)	$\lambda_{\text{max,PL}}$ (nm/eV)
Poly(BFMP$_{12}$-AV)	299/4.16	338/3.66
KPD-1	322/3.83	374/3.31
Poly(BFMP$_{12}$-AV) : KPD-1 99 : 1 (w/w)	309/4.01	564/2.19
Poly(BFMP$_{12}$-AV) : KPD-1 97 : 3 (w/w)	305/4.06	586/2.11
Poly(BFMP$_{12}$-AV) : KPD-1 95 : 5 (w/w)	305/4.06	565/2.19

0.183 lm/W (12 V). The luminance efficiency (η, lm/W) was calculated by using the following equation:

$$\eta = (\pi L)/(VJ) \tag{1}$$

where L(cd/m^2), V(V), and J(A/m^2) are luminance intensity, applied voltage, and current density, respectively. This result indicated that hole and electron trnasporting rate in D-2 device was well balanced by introducing Alq$_3$ as an ETL. As presented in Figure 3, D-2 device also exhibited $\lambda_{\text{max,EL}}$ 604 nm, longer wavelength than other PLEDs. EL emission colors of

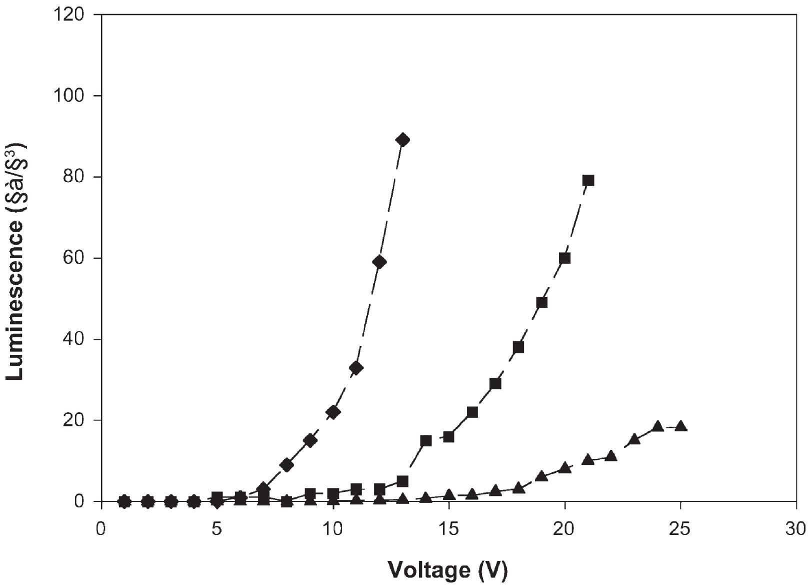


FIGURE 2 Luminance vs. voltage profile of single- and double-layered PLEDs; S-2 (■), D-1 (▲, D-2 (◆).

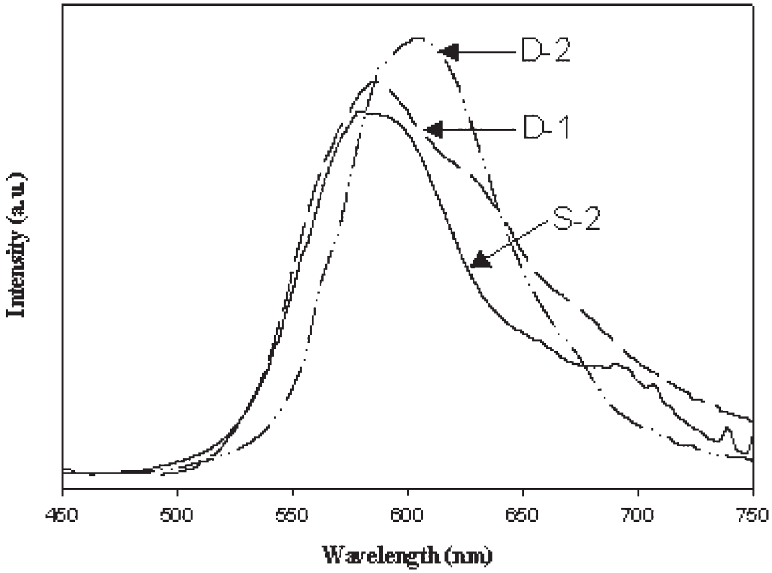


FIGURE 3 EL spectra of single- and double-layered PLEDs.

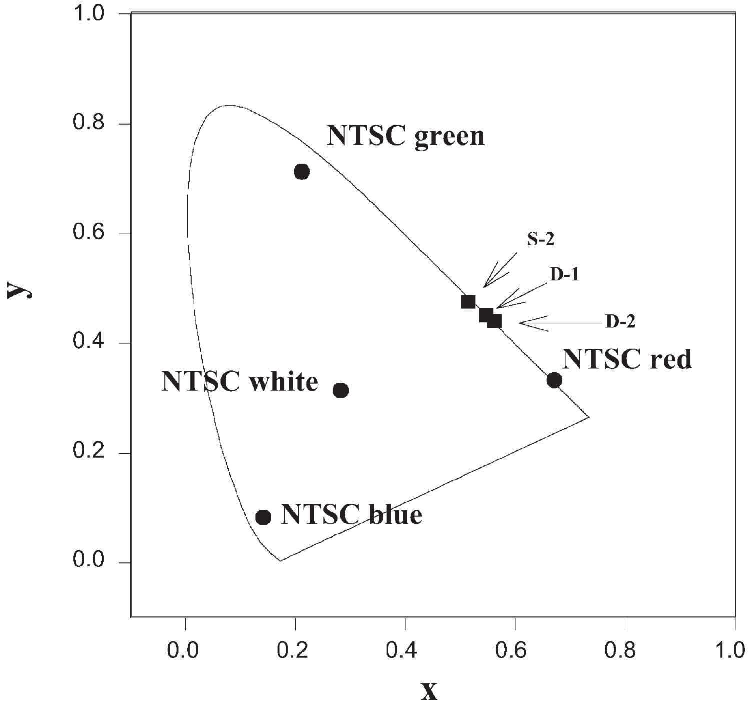


FIGURE 4 Color coordinates of PLEDs.

PLED's are shown in Figure 4, according to the NTSC chromaticity diagram. The EL emission of PLED's showed green ($x = 0.5128$, $y = 0.4730$) for S-2, yellowish-orange ($x = 0.5455$, $y = 0.4485$) for D-1, and orange ($x = 0.5605$, $y = 0.4380$) for D-2 devices, respectively.

CONCLUSIONS

KPD-1 dopant possessing both phenothiazine and antracene moieties were synthesized by using Horner-Emmons reaction and were used as a dopant in the polymer matrix, poly($BFMP_{12}$-AV). The optimized weight ratio of poly($BFMP_{12}$-AV)/KPD-1 (97/3 w/w) dopant system exhibited a maxium red-shift of PL emission. PLEDs were fabricated with the same composition of matrix/dopant as a light emitting layer. Double-layered ITO/[poly ($BFMP_{12}$-AV)/KPD-1]/Alq_3/Al (D-2 EL device), which contained Alq_3 layer as an ETL, exhibited enhanced EL emission and efficiency compared to those of other PLEDs by stopping the holes transported and enhancing injection of electrons to the emitting layer.

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