

# Synthesis and luminescent characteristics of novel phosphorus containing light-emitting polymers

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## Abstract

Organic light-emitting diodes (OLEDs) have been developed recently, however, the efficiency of electroluminescent devices needs to be further improved. In this study, the electron-transporting chromophores were introduced into an emission polymer to increase its electron affinity. Several phosphorus-containing emission chromophores were synthesized and incorporated with electron-transporting chromophores. The effect of different structures on the optoelectric properties was investigated in detail.

2,5-Bis-(4-fluorophenyl)-1,3,4-oxadiazole and 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) derivatives were used as electron transport and emission monomers, respectively. The DOPO derivatives that contain benzene, biphenyl or 1,4-naphthalene were synthesized. The emission chromophores emit blue light as expected. Aromatic polyethers were obtained by nucleophilic substitution reaction of oxadiazole-activated bis(halide) monomers with bis(phenol) monomers. All the resulting polymers were thermally stable below 450°C. The absorption peaks of these polymers varied from 325 to 350 nm, while the photoluminescent peaks varied from 377 to 464 nm. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Organic light-emitting diodes; Polymer; Oxadiazole

## 1. Introduction

Light-emitting diodes (LEDs) are extremely important optoelectronic materials and have been applied in a variety of products such as electronic and optoelectric commercial products. Although the flat panel displays that utilize electroluminescent technology have already been on the market [1] since 1997, they are all made by using small molecule [2,3]. For example, Pioneer Company's green electroluminescent has used quinacridone. However, for better luminescence efficiency or intensity, all the fluorescence dyes of small molecule have to be mixed with other materials. The mixed materials have such bad compatibility that they bring about detachment between the mixed materials. Furthermore, the process of using vapor deposition procedure to produce light-emitting devices is quite complicated and it is very difficult to make panels with large area using this process. Since the discovery by Holmes and others in the UK [4] of the electroluminescent characteristics, many polymers that can be used to fabricate LEDs have been synthesized [5] to compensate for the drawbacks

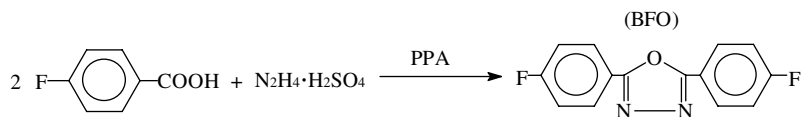
of liquid crystals which pose difficulties in the fabrication of large-area display panels.

The electroluminescence (EL) devices using an organic dyes are made by vacuum technique, which lines up the molecule very regularly in films and results in lesser number of traps in the films. Thus, they have high luminescent efficiency. They are, however, not stable and have weak mechanical strength. The molecule of a polymer is very difficult to purify and to line up regularly and also contains lots of traps. So the electrons and holes are easy to be captured by traps, and thus will result in a loss of energy [6].

In the 1990s, Holmes and others first discovered electroluminescent materials by means of poly(1,4-phenylene vinylene) (PPV) which can emit green-yellow light (peak wavelength between 520 and 551 nm) [7,8]. PPV has the advantages of being lightweight, having large size, flexibility and ease of fabrication into flat panel displays, which are the general properties of polymeric materials. PPV's tensile strength is better than that of polyaramide and can survive severe conditions during device processing.

The solubility of PPV is generally very low. So it is difficult to fabricate a thin film by spin coating technique. The solubility is greatly increased if the PPV polymers

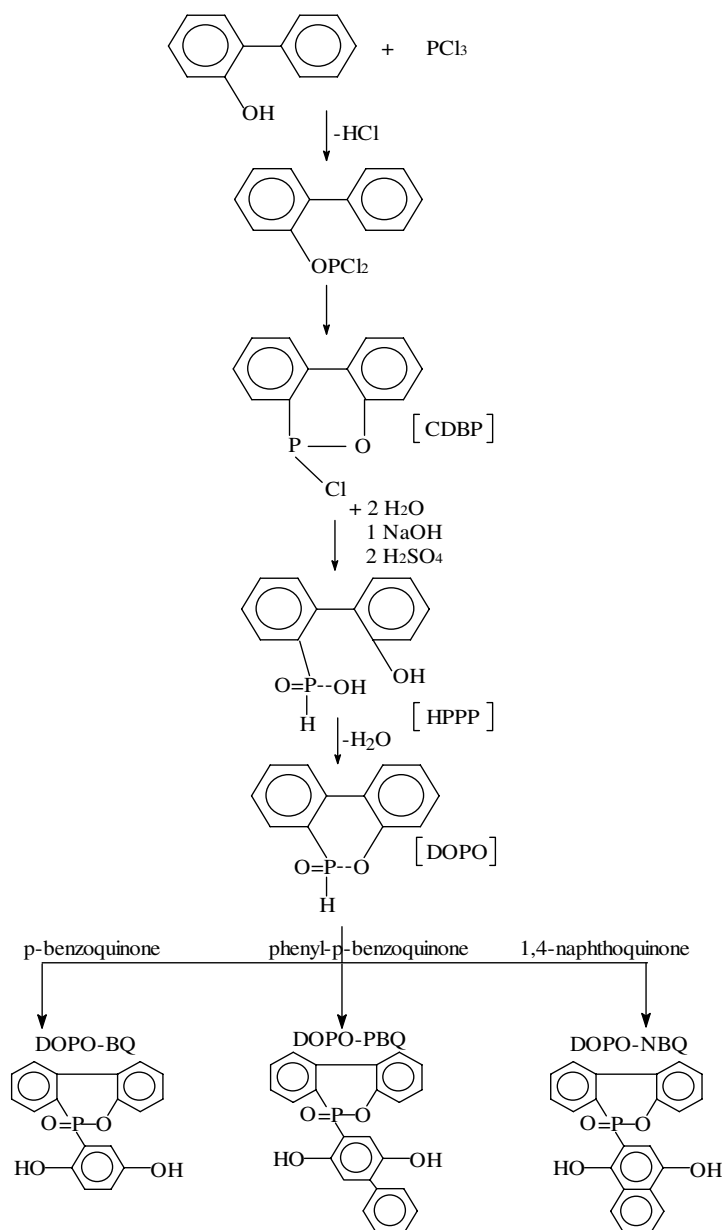
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Scheme 1.

contain a bulky side-chain, such as poly(2,5-dialkoxy-*p*-phenylene vinylene) (RO-PPV) [9,10]. The incorporation of bulky, thermally stable and flame retardant DOPO into the polymer side-chain was thought to increase the solubility and thermal stability of the resulted polymers. In this study, several novel phosphorus-containing emission chromophores were synthesized and incorporated with electron-transporting chromophores. The effect of structures

on the optoelectric properties will be investigated in detail. We take the advantages of the polymers with emission chromophores to improve upon the drawbacks of all conjugated polymers that show photoluminescence in the long wavelength range. This experimental system chooses the electron affinity group of 2,5-diphenyl-1,3,4-oxadiazole that has good thermal stability, but generally has poor solubility in solvent [11]. In the 1960s, Johnson synthesized aromatic



Scheme 2.

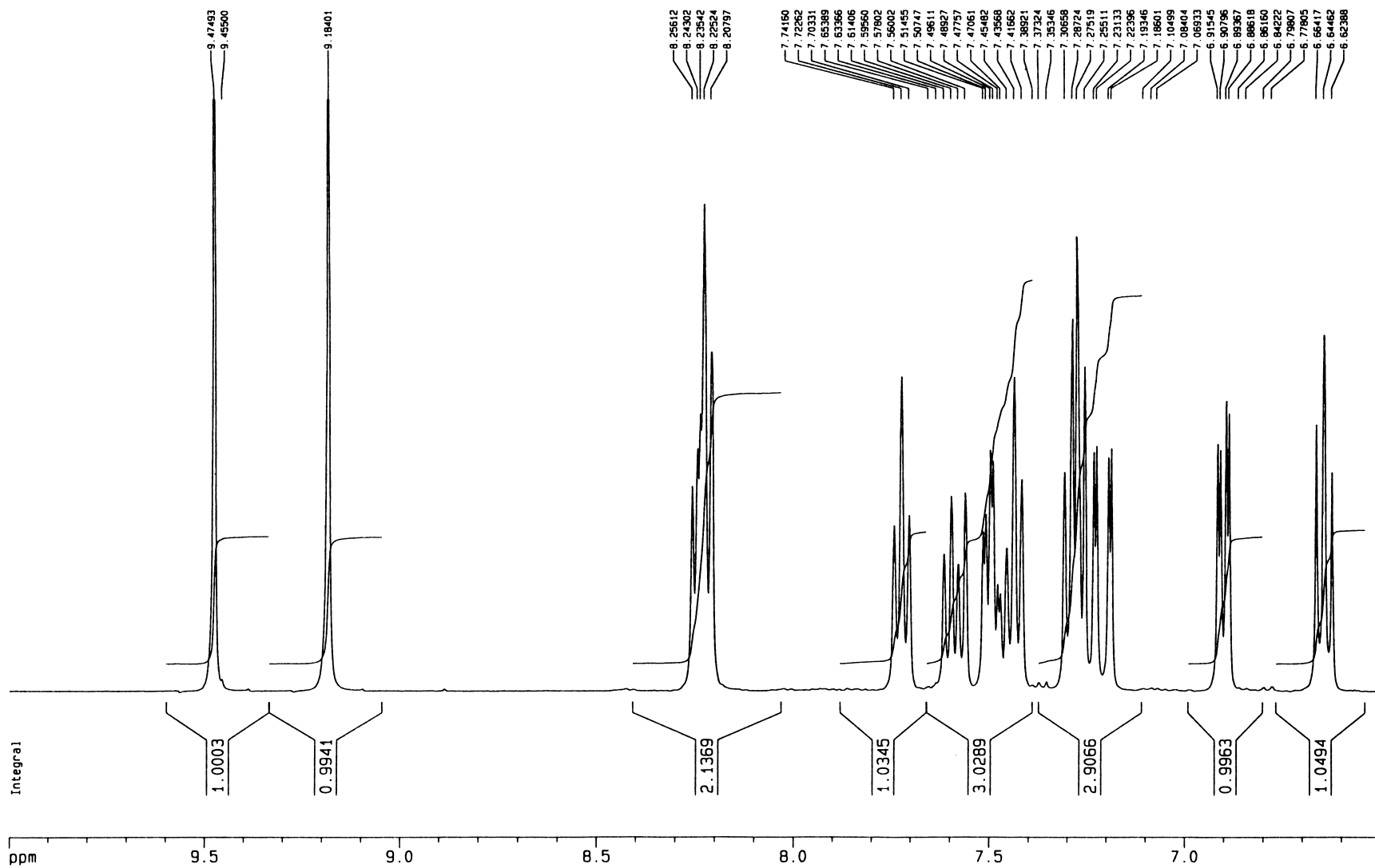


Fig. 1.  $^1\text{H}$  NMR spectrum of 2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)-1,4-benzenediol (DOPO-BQ).

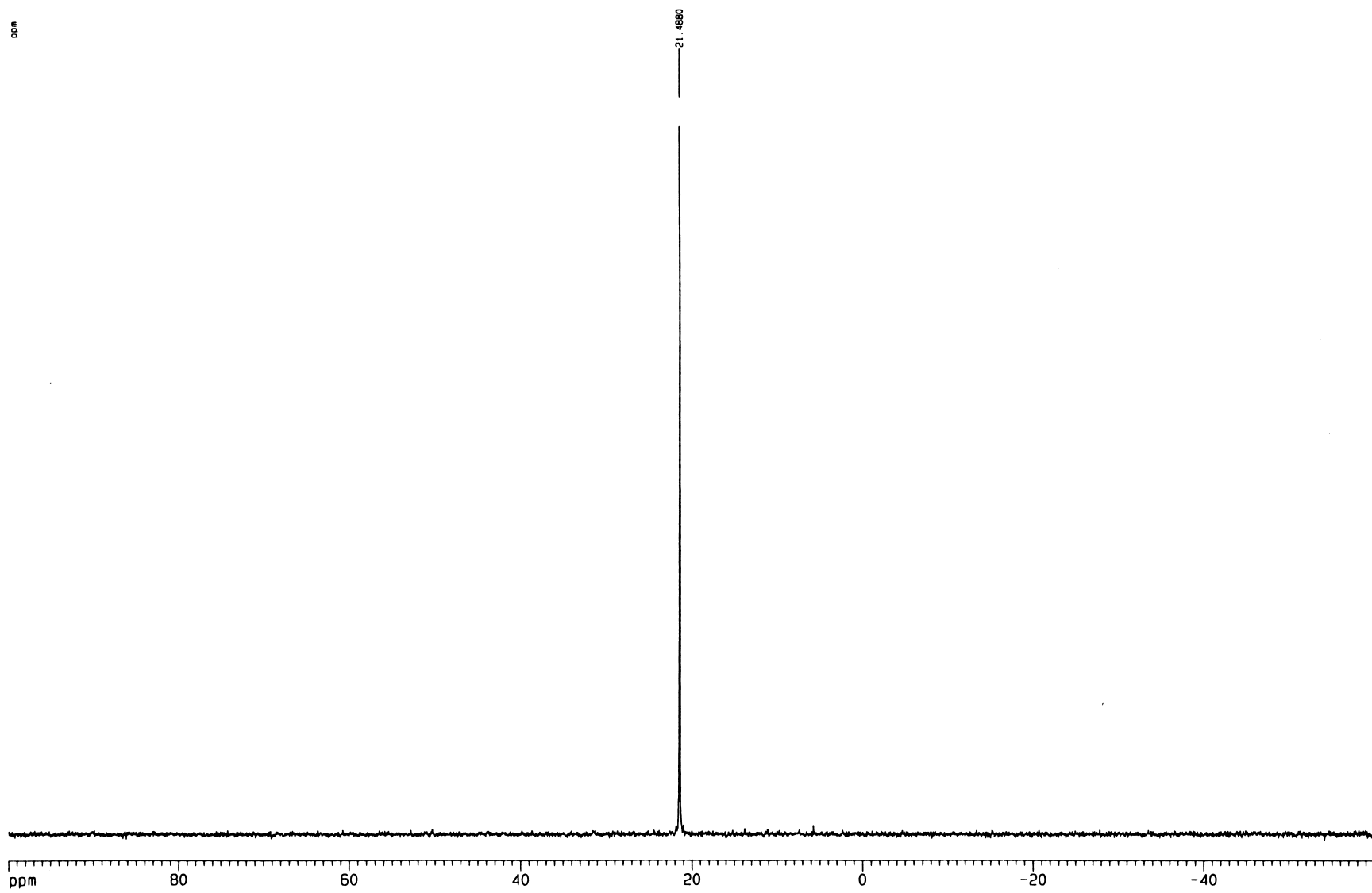
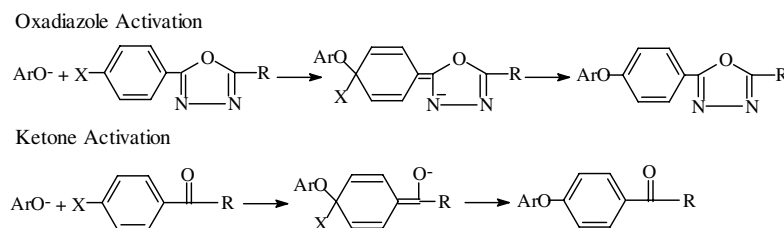


Fig. 1. (continued)



Scheme 3.

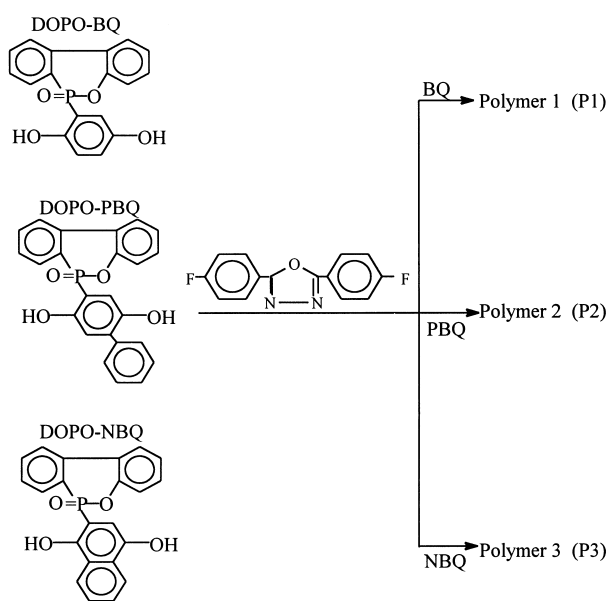
polyethers containing 2,5-diphenyl-1,3,4-oxadiazole [12], and discovered that using this aromatic ether as spacers not only increased the solubility of polymer but also resulted in good thermal stability. Therefore in this research, 2,5-bis-(4-fluorophenyl)-1,3,4-oxadiazole was incorporated with three derivatives of 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) to provide electron-transporting chromophores and emission chromophores.

## 2. Experimental

### 2.1. Materials and measurements

All reagents and solvents were reagent grade or were purified by standard methods before use. *o*-Phenyl phenol, phosphorus trichloride, *p*-benzoquinone (BQ), phenyl-*p*-benzoquinone (PBQ) and 1,4-naphthoquinone (NBQ) from Aldrich Co. were used as received. Ethylene glycol monoethyl ether (ethoxyethanol), *N*-methyl-2-pyrrolidone (NMP), *N*-cyclohexyl-2-pyrrolidone (CHP) and methanol from Acros Co. were used as solvent and purified before use.

Elemental analyses were performed by the Heraeus



Scheme 4.

CHN-O-Rapid elemental analyzer. FTIR spectra were recorded with a Nicolet 5DX-B spectrophotometer. Mass spectra were recorded by the VG 70-250 S GC/MS (mass spectrometer). Melting points of monomer were determined with a polarizing microscope (Laboratory Devices MEL-TEMPPII). The thermal behavior of each polymer was studied on a Perkin-Elmer DSC7 and TGA7.  $^1\text{H}$  nuclear magnetic resonance (NMR) was performed in  $\text{CF}_3\text{COOD}$  or DMSO at  $50^\circ\text{C}$ . UV-Vis spectra were obtained with a Perkin-Elmer Lambda 9 spectrometer. Optical characterization was performed by photoluminescence (PL) measurements, where the 325 nm line of He-Cd laser with 20 mW power was used to excite the sample.

### 2.2. Synthesis of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole (BFO)

To a 250 ml reaction vessel equipped with a temperature controller and overhead stirrer was added 6.574 g hydrazine sulfate, 14.8 g 4-fluorobenzoic acid and 100 g polyphosphoric acid. The mixture was first heated slowly to  $80^\circ\text{C}$  to dissolve the reactants. Then the reaction mixture was heated at  $150^\circ\text{C}$  for 8 h. The mixture was further heated at cyclization temperature ( $200^\circ\text{C}$ ) for another 2 h. After completion of the reaction, the mixture was precipitated into 500 ml of deionized water. The precipitate was recrystallized from methanol and dried. Yield 76%; m.p.  $204\text{--}205^\circ\text{C}$ . The IR spectrum (KBr) exhibited absorptions at 3058, 1607 ( $\text{--C=N--}$ ), 1493, 1226, 1160, 1093, 1070, 845,  $745\text{ cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_2\text{F}_2$ : C, 65.12; H, 3.15; O, 6.19; N, 10.85. Found: C, 65.15; H, 3.12; O, 6.20; N, 10.86. EIMS;  $m/z$ : 258(83,  $\text{M}^+$ ). The synthesis procedure is shown in Scheme 1.

### 2.3. Synthesis of 2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl) derivatives (DOPO-BQ, DOPO-PBQ, DOPO-NBQ)

Derivatives of DOPO were synthesized according to our previously published procedures [13] as shown in Scheme 2. The DOPO derivatives were further recrystallized from ethoxyethanol. Yield is typically 70%.

2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)-1,4-benzenediol (DOPO-BQ); m.p.:  $245\text{--}246^\circ\text{C}$ . IR (KBr): 1168, 925 ( $\text{P--O--Ph}$ ), 1190 ( $\text{P=O}$ ), 1348 ( $\text{P--OH}$ ), 3173 ( $\text{Ph--OH}$ ),  $1582\text{ cm}^{-1}$  ( $\text{P--Ph}$ ). The shift and splitting pattern of  $^1\text{H}$  NMR spectrum is 6.69 (t, 1H), 6.93 (dd, 1H), 7.16 (dd, 1H), 7.24–7.34 (m, 2H), 7.40–7.51 (m, 2H), 7.66–7.76

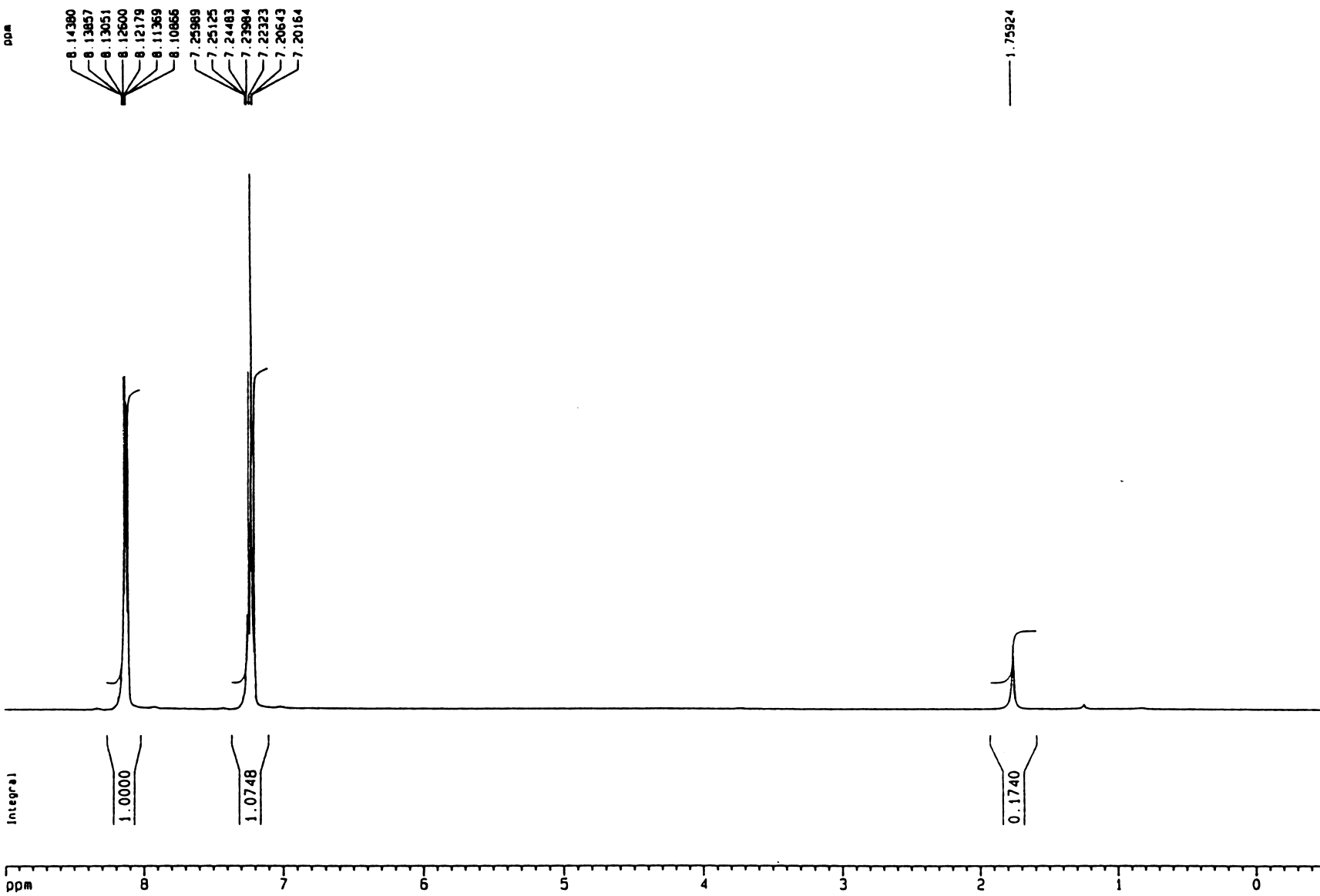


Fig. 2.  $^1\text{H}$  NMR spectrum of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole.

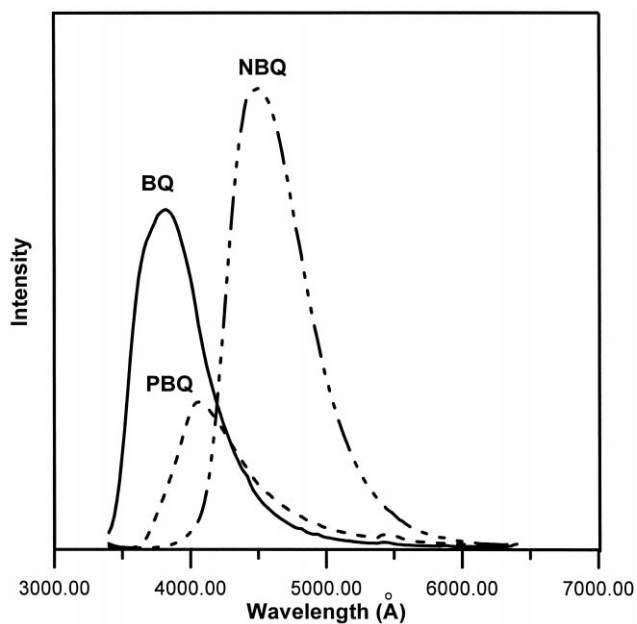


Fig. 3. The photoluminescence spectra of the DOPO derivatives.

(m, 2H), 8.13–8.19 (m, 2H), (Fig. 1),  $^{31}\text{P}$  NMR (DMSO): a single peak at  $\delta = 2.15$  ppm (Fig. 1). Anal. Calcd. for  $\text{C}_{18}\text{H}_{13}\text{O}_4\text{P}$ : C, 66.67; H, 4.04; O, 19.74; P, 9.52. Found: C, 66.57; H, 4.10; O, 20.04; P, 9.29. MS  $m/z$ : 324(100,  $\text{M}^+$ ).

2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)-phenyl-1,4-benzenediol (DOPO-PBQ), m.p.: 117–118°C; 2-(6-oxido-6H-dibenz(c,e)(1,2)oxaphosphorin-6-yl)-1,4-naphthalenediol (DOPO-NBQ), m.p.: 279–280°C. The structures of DOPO-PBQ and DOPO-NBQ were also confirmed by elemental analyses, IR and NMR spectra. The spectrum of DOPO-NBQ is analogous to that of DOPO-BQ and shows the expected single peak in the  $^{31}\text{P}$  NMR spectra.

#### 2.4. Synthesis of organic light-emitting polymer containing phosphorus

To a 200 ml reaction vessel equipped with a temperature controller, overhead stirrer and a Dean–Stark trap was charged with 1 mmol of the respective monomers, 2.2 mmol  $\text{K}_2\text{CO}_3$ , 15 ml toluene and 5 ml NMP/CHP (vol. ratio 1:1). The mixture was heated to 140°C for 3 h under intensive stirring. Then excess xylene was removed and the reaction mixture was heated at reflux (160–190°C) for 24 h. After cooling under nitrogen, the mixture is poured into

400 ml acetone/methanol (vol. ratio 1:1) with addition of 5 ml NMP. The mixture was further stirred at room temperature for 24 h. The precipitate was collected, washed with distilled water, extracted with chloroform and dried under vacuum. After drying the polymers were obtained as gray solids.

### 3. Results and discussion

In this study, polymers containing electron-transporting chromophores and emission chromophores in the main chain were synthesized. The emission wavelengths of these synthesized polymers were adjusted by varying the molecular structures. The synthetic strategy of the desired monomers from simple starting materials is outlined in Schemes 1 and 2. The structures of these products were characterized by IR, NMR spectroscopies, elemental analysis and by DSC and TGA to analyze the thermal properties of these polymers. The optical properties including absorption and luminescence of these polymers were measured with UV–Vis and PL systems.

#### 3.1. Monomer syntheses and characterization

Two kinds of monomers were synthesized. 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (BFO) is the electron-transporting chromophore in polymers. Since 1,3,4-oxadiazole is a heterocyclic compound with less electrons, it can increase the electron affinity of the polymers. The other advantage is that it can disperse negative charges in the transition state when aromatic polyethers were synthesized, so the transition state would be stable and the reaction could be carried out more easily. As shown in Scheme 3, the ketone group activates X in this reaction, the 1,3,4-oxadiazole can also activate the *ortho*- and *para*-substitution group in this reaction.

Fig. 2 shows the  $^1\text{H}$  NMR spectrum of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole. The hydrogens of the aromatic ring neighboring with 1,3,4-oxadiazole are located at  $\delta = 8.1$  ppm. If 1,3,4-oxadiazole is replaced by ketone group, the  $^1\text{H}$  NMR peak will shift to about 7.9 ppm, the same as those shown in the Aldrich Library of NMR Spectra. This result indicates that the 1,3,4-oxadiazole has stronger nucleophilic affinity than that of ketone and makes the reaction more facile, an effect which occurs in other systems of heterocyclic compounds, such as triazoles, triazines, etc.

In this study, the DOPO derivatives were used as emission

Table 1

The polymerization results (the conditions of polymerization are 180°C, 24 h) of P1 with different solvents (++, soluble at room temperature; (+–), partially soluble on heating; ––, insoluble)

Solvent	$\eta$ (dl/g) <sup>a</sup>	NMP	DMSO	Pyridine	Xylene	DMAC
Diphenyl sulfone	0.24	++	++	++	--	++
NMP/CHP	0.51	++	--	--	--	+–

<sup>a</sup> Intrinsic viscosity is measured at 30°C in NMP.

Table 2  
Polymerization conditions and results of polymers P1–P3

Items	P1	P2	P3
Reaction temperature (°C)	180	160	190
Reaction time (h)	24	24	24
Solvent	NMP/CHP	NMP/CHP	NMP/CHP
Yield (%)	71	76	77
Intrinsic viscosity (dl/g)	0.51	0.54	0.49
Calc. <sup>a</sup>	C <sub>32</sub> H <sub>19</sub> N <sub>2</sub> O <sub>5</sub> P	C <sub>38</sub> H <sub>23</sub> N <sub>2</sub> O <sub>5</sub> P	C <sub>36</sub> H <sub>21</sub> N <sub>2</sub> O <sub>5</sub> P
Found <sup>b</sup>	C <sub>32.3</sub> H <sub>19.5</sub> N <sub>2.1</sub> O <sub>5</sub> P	C <sub>39.1</sub> H <sub>23.4</sub> N <sub>2.2</sub> O <sub>5</sub> P	C <sub>36.8</sub> H <sub>22.3</sub> N <sub>1.9</sub> O <sub>5</sub> P

<sup>a</sup> Molecular formula of repeating unit.

<sup>b</sup> Molecular formula of repeating unit was characterized by elemental analysis.

chromophores in the polymer. The DOPO derivatives include benzene, biphenyl or naphthalene ring structure as luminescent units. The PL spectra of the DOPO derivatives are shown in Fig. 3. The peak luminescent wavelengths are 388, 405 and 450 nm for DOPO-BQ, DOPO-PBQ and DOPO-NBQ, respectively. It is apparent that the naphthalene ring has shifted the wavelength more towards the red than biphenyl ring because of its conjugated nature. The results are in agreement with our expectation that the spectra of DOPO-PBQ and DOPO-NBQ should emit light in the blue emission region. Therefore, the DOPO series can be adapted as precursors for organic light-emitting materials.

### 3.2. Synthesis of organic light-emitting polymer and characterization

In order to understand the physical and optical properties of the synthesized polymers, three kinds of polymers, P1, P2 and P3 were synthesized (Scheme 4). The effects of the extended rings, benzene, biphenyl and naphthalene on the luminescent properties were studied. Polymers were synthesized by means of the activation of phenolic OH group with K<sub>2</sub>CO<sub>3</sub>. The nucleophilic substitution reaction occurred in the mixed solvent of CHP and NMP. The CHP was added into the solvent to avoid the side reaction because CHP becomes insoluble in water when the reaction temperature was higher than 80°C. In Ref. [14], the high molecular weight and high solubility aromatic polyether was obtained when diphenyl sulfone was used as a solvent. Table 1 compares the results of P1 synthesized from these two solvent systems. From the intrinsic viscosity and solubility

of P1, it is apparent that the high molecule weight polymer can be obtained with the NMP/CHP solvent mixture. Our results are contrary to those shown in Ref. [14]. The reaction conditions and results are listed in Table 2. Transparent films can be obtained by spin coating of the polymer solution. The solubilities of the polymers in various solvents are listed in Table 3. All polymers are not soluble in high polar solvent like DMSO. The polymer P2 has better solubility because of its non-planar benzene ring in the side chain which increases the free volume of the polymer.

### 3.3. Thermal analysis of the polymers

When the polymer LED devices operate at some voltage, the temperature of the device will increase. So the thermal stability of polymers is very important.  $T_g$  of polymers must be as high as possible to avoid the loss of mechanical strength when the operating temperature is high. If the polymer crystallizes, it may be separated in phases, thereby reducing the device efficiency.

DSC and TGA are the most favored techniques for rapid evaluation and for comparing and ranking the thermal stability of various polymers. Table 4 shows that polymers with DOPO and 1,3,4-oxadiazole ring have  $T_g$ s in the range of 230–260°C and no  $T_m$  peak is seen even after the temperature rises above 320°C. The  $T_g$  for P2 and P3 are 231 and 262°C, respectively. Both P2 and P3 have higher  $T_g$  than P1 (228°C) due to their bulkier nature or because they have more rigid groups in the side- or main chain.

From the results of TGA as shown in Fig. 4, it is apparent that these polymers have excellent thermal stability. The

Table 3  
Solubilities of polymers (++, soluble at room temperature; +-, partially soluble on heating; --, insoluble)

Sample	DMSO	DMAC	NMP	Pyridine	CHCl <sub>3</sub>	THF	Toluene
$E_T$ (30) <sup>a</sup>	45.1	43.7	42.2	40.5	39.1	37.4	33.9
P1	--	++	++	++	+–	--	--
P2	--	++	++	++	++	+–	--
P3	--	+–	++	--	--	--	--

<sup>a</sup> The polar parameter of solvent (kcal/mol):  $E_T = hc\nu/N_A$ .

Table 4  
Thermal properties of the polymers P1–P3

No.	$T_g^a$ (°C)	$T_m$ (°C)	$T_d^b$ (°C)
P1	228	–	505
P2	231	–	525
P3	262	–	560

<sup>a</sup> Determined by DSC at a heating rate of 20°C/min.

<sup>b</sup> Temperature at which 10% weight loss was recorded by means of TGA at a heating rate of 50°C/min.



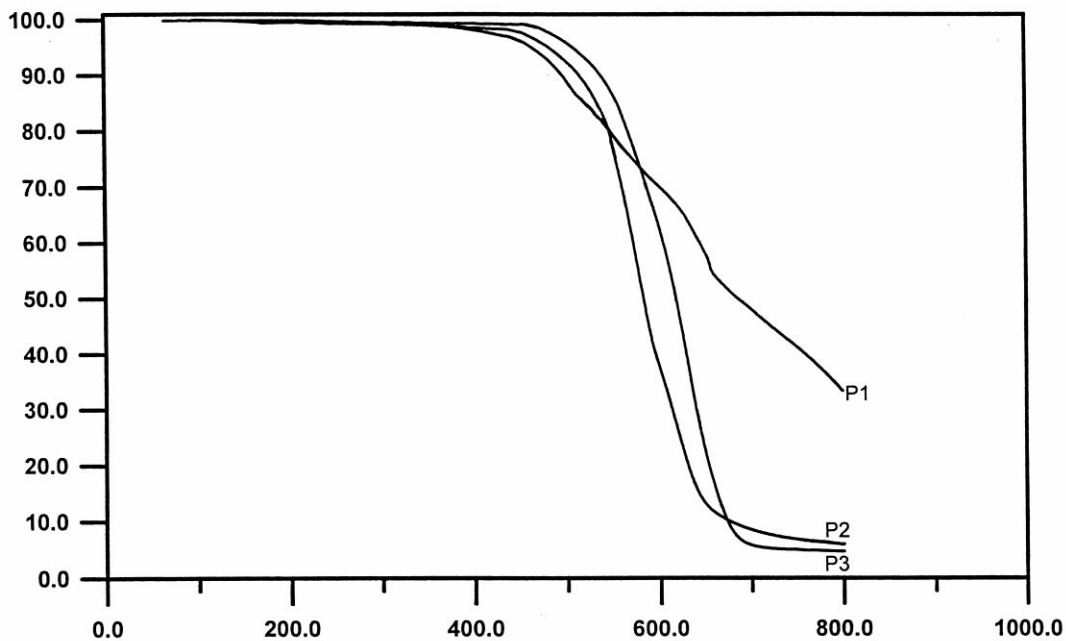


Fig. 4. TGA thermograms of P1–P3.

starting temperatures of degradation are all higher than 480°C for P1–P3. The drastic decrease in weight was observed when the temperature was close to 480°C which may be due to the degradation of the DOPO chain.

### 3.4. Optical properties

The emitting wavelengths of the EL polymers depend on the structure of the polymers. The absorption and PL spectra were measured. Figs. 5 and 6 show the UV–Vis absorption spectra of the polymers in solution and as thin films, respectively. The peak absorption wavelengths are shown in Table 5. From Table 5, it is found that the polymer solution has

apparently shifted the wavelength more to blue than thin film type which may be attributed to the expansion of polymer chain in the solvent. The aggregation effects of polymers in thin film will make the energy band gap of polymers narrower than in solution and the wavelength will shift toward red. The phenomenon is in agreement with Ref. [15]. The variation of energy band gap in polymers is not only due to the variation of molecular distances but also due to the polarity of solvents. Table 6 shows the UV–Vis absorption peak values for the polymers dissolved in various solvents with different polarity. The peak absorption wavelengths did not increase with increasing polarity. It shifted to red first and then to blue because the highly polar solvent

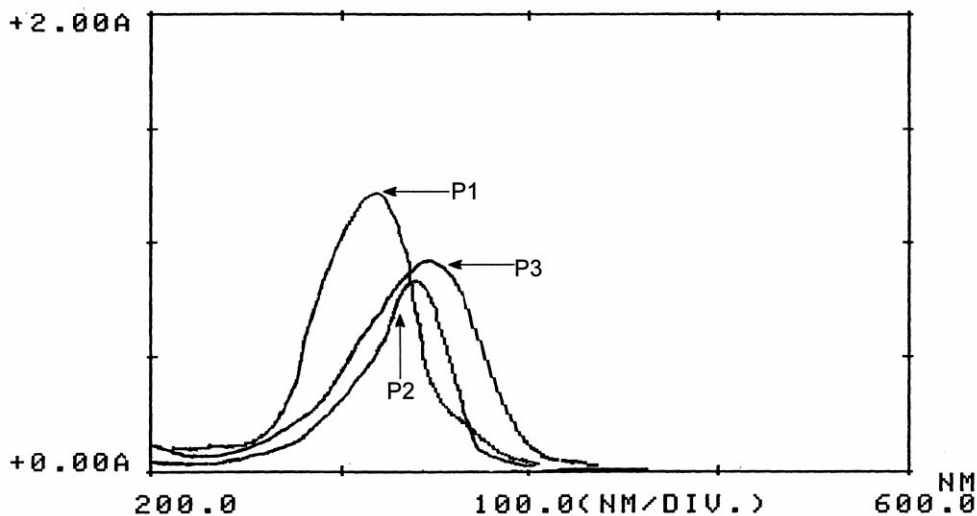


Fig. 5. UV–Vis absorption spectra of P1–P3 in the solution state.

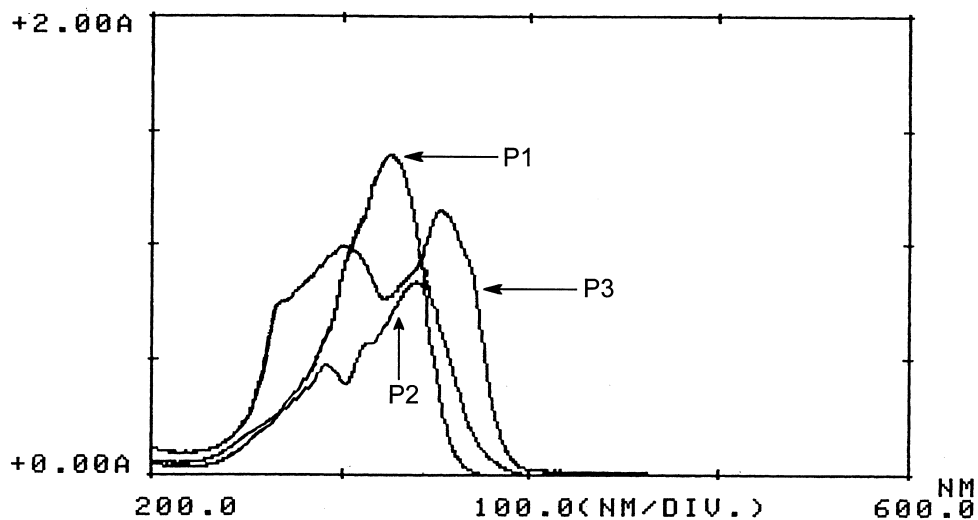


Fig. 6. UV-Vis absorption spectra of P1–P3 as thin films.

produced the orientation polarization effect and generated an electrical field with emission chromophores. The electrical field changes the basic state of the molecules. In Ref. [16], the similar phenomenon was discussed but the shift was only a few nanometers in this study. It is mainly due to the absence of strong donor–acceptor pairs in the emission chromophores. Although the oxygen atoms have unshared electron pairs, they are not strong donors. Another reason is

that a polymer is not as easy as a small molecule to be surrounded by solvents. These reasons made the absorption spectra shift less.

The PL spectra of the polymers are shown in Fig. 7. The luminescent peak wavelengths are shifted to longer wavelengths with increasing conjugating rings. The peak wavelengths are shown in Table 5. Although both P2 (with biphenyl) and P3 (with naphthalene) have two

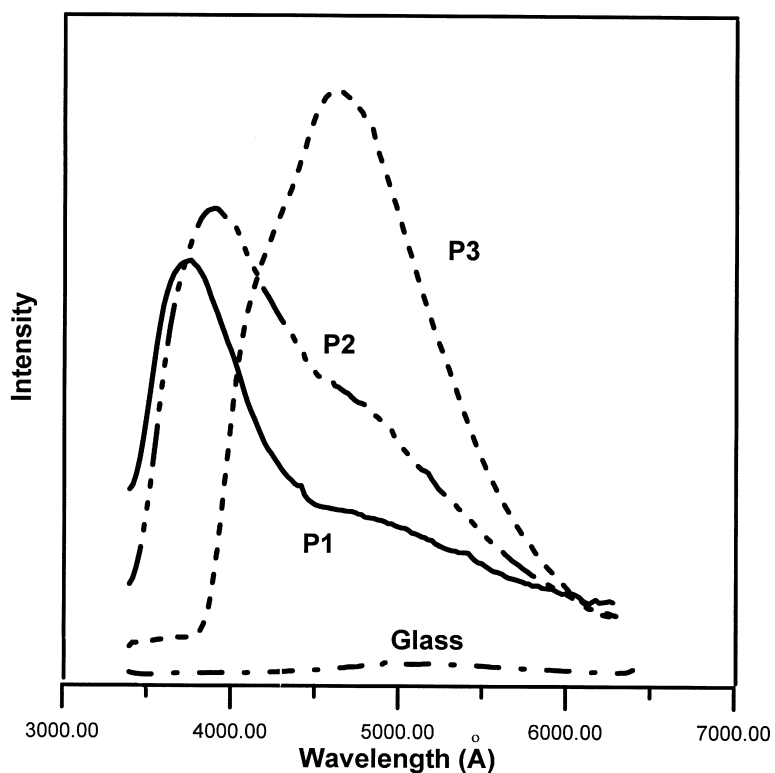


Fig. 7. The photoluminescence spectra of the polymers.

Table 5

The absorption and photoluminescent maxima (in nm) of P1–P3 in film or solution states at room temperature

No.	UV <sub>(solvent)</sub>	UV <sub>(film)</sub>	PL <sub>(film)</sub>	Stokes shift <sup>a</sup>
P1	325 (NMP)	328	377	49
P2	338 (NMP)	344	391	47
P3	345 (NMP)	350	464	114

<sup>a</sup> Stokes shift (in nm) = PL<sub>(film)</sub> – UV<sub>(film)</sub>.

conjugating rings, the PL peak of P2 is shorter than P3 by 73 nm. It is due to the existence of a stereo torque angle between two benzene rings that breaks the conjugation plane and shortens the conjugation length. The luminescent wavelength of P2 was similar to P1 in red wavelength but shifted by 14 nm. The peak wavelength of P3 with naphthalene rings shifted 87 nm toward red relative to P1. It is seen that the conjugation effect from the biphenyl is much less than that from the naphthalene. All the polymers had pure luminescent spectra without other shoulder peaks due to the possession of only one kind of emission chromophore, therefore, the degree of polymerization had no effect on the width of the luminescent spectra. In Table 5, the Stokes shift is the difference between PL and UV–Vis absorption peaks. If the Stokes shift is too small, the emission and absorption spectra will overlap more. Then the emitting light will be self-absorbed and the luminescent efficiency will decrease in the devices. Due to the big Stokes shift of P3, it is the best material of the polymers evaluated for organic light emitting diodes.

The relative PL efficiencies of our novel polymers and the commercialized RO-PPV (poly(2-methoxy-5(2'-ethylhexylexy)-*p*-phenylene vinylene) made by Sumitomo Chemical Co. Ltd.) are ~16 and ~10% to that of PPV, respectively.

#### 4. Conclusions

Several phosphorus-containing emission chromophores were synthesized and incorporated with electron-transporting chromophores. The physical properties of the polymers were successfully modified by the incorporation of DOPO and using moldability of aromatic ether as a spacer, so they generally showed better solubility and greater thermal stability. Moreover, the effects of structures on the optoelectric properties were investigated. The luminescent wavelength

Table 6

UV–Vis absorptions of P1 and P2 in different polar solvents at room temperature (–: insoluble)

	λ <sub>max</sub> (nm)					
	Toluene	THF	CHCl <sub>3</sub>	Pyridine	NMP	DMAC
Solvent polarity	Low	→				High
P1	–	–	326	329	325	322
P2	–	–	329	333	336	338

of P2 is similar to P1, while the peak wavelength of P3 with naphthalene ring shifts 87 nm towards red relative to P1. It is seen that the conjugation effect from the biphenyl is much less than that from the naphthalene.

#### Acknowledgements

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