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Synthesis and optical properties of novel blue light-emitting polymers with electron affinitive oxadiazole

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Abstract

A series of novel polyethers, which can be used as a blue electroluminescent material were prepared from two diarylethylene-containing emission chromophores with two oxadiazole-containing electron-transporting chromophores. The characterization and effect of different structures on optoelectric properties was investigated by use of thermal analysis and spectroscopy (infrared, ultraviolet-visible, photoluminescence, cyclic voltammetry) measurement.

2,5-Bis-(4-fluoroaryl)-1,3,4-oxadiazole and 4,4′-dihydroxyarylethylene were used as electron transport and emission monomers, respectively. The 4,4′-dihydroxyarylethylene derivatives that contain benzene–benzene and benzene–naphthalene were synthesized by Horner–Wadsworth–Emmons olefination reaction. 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. Moreover, two polymers containing hexaethylene chain instead of electron transport unit were also synthesized for comparison. All the resulting polymers containing oxadiazole group were thermally stable below 470°C. The absorption peaks of these polymers varied from 310 to 370 nm, while the photoluminescent peaks varied from 377 to 456 nm. These polymers containing electron-transporting oxadiazole indeed show extra reduction potentials in CV measurements. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: P-LED; Diarylethylene; Oxadiazole

1. Introduction

Light-emitting diodes (LEDs) are extremely important optoelectronic materials and have been applied in various 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 molecules [2,3]. For example, Pioneer Company's green electroluminescence has used quinacridone. However, for better luminescent efficiency or intensity, all the fluorescent dyes of small molecules have to be mixed with other materials. The mixed materials are so incompatible 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 a large area.

Polymers with extended π-systems are attractive for a wide range of potential applications from antielectrostaic coatings and biosensors to solar cells, photonic switching, light-emitting and molecular electronic devices [4–6]. In particular, π-conjugated polymers have been considered as organic light-emitting materials for the fabrication of electroluminescent devices. The primary reason is the high photoluminescent (PL) quantum yields in the visible region which characterize many of these materials, combined with the advantage of simple processability into flexible, mechanically robust films or thin layers. The conjugated polymers are favored as emitting layers for polymer based LEDs, particularly poly(*p*-phenylenevinylene) (PPV) [7], poly(*p*-phenylene) (PPP) [8,9] and polythiophene [10] type.

Since the Cambridge group [7] found that PPV can be used as a light-emitting layer for LEDs in 1990, polymer organic LEDs have drawn great attention and been synthesized one after another in the past few years [11]. Because semiconducting polymers possess several advantages over inorganic semiconducting materials, such as low cost, easy processability, flexibility [12] and ease of forming large area [13], etc., polymer LEDs exhibit considerable promise in the applications of electroluminescence displays and backlight source for liquid crystal display.

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The advantage of organic light emitting diodes (OLEDs) is to change the wavelength of luminescence by special molecular design that can adjust the energy band gap between LUMO and HOMO. The energy band gap of polymer depends on the conjugated length. When the conjugated length is longer and the energy band gap is lower, the wavelength will shift toward red [14]. On the contrary, shorter conjugated length will make the wavelength shift toward blue. The steric hindrance and twist angle between rings will reduce the conjugation effect, which result in the higher energy band gap. So there are two methods to change the band gap. The first method is to introduce a bulky side chain to increase steric hindrance and twist angle, which will enlarge the band gap. The second method is to decrease the twist angle by rigid aromatic ring and make the conjugated length increase. In addition, we can increase the solubility and control the luminescent wavelength by non-conjugated spacer to connect emission chromophores having different conjugated lengths. These non-conjugated spacers include ether group, ester group, amide group, … etc [15].

The ideal OLED does require not only its property of luminescence, but also, the efficiency of electroluminescent devices to be further improved. Some effective methods have been developed for improving the performance by increasing the efficiency of the recombination of electrons and holes. One way is to add an electron-transport layer in between the emitting layer and cathode allowing a balance of charge injection and transport by enhancing the transport of electrons and in some occasions blocking the transport of holes so that the recombination zone is kept away from the interface near cathode. In recent years, both low molecular weight oxadiazole derivatives and oxadiazole-containing polymers [16–18] have shown to provide improved quantum efficiency and are often regarded as electron transport layer (ETL).

In this study, two novel diarylethylene-containing emission chromophores were synthesized and incorporated with electron transporting chromophores. The effect of structures on optoelectric properties will be investigated in detail. We take the advantages of the polymers with emission chromophores to improve the drawbacks of all conjugated polymers that emit photoluminence in the long wavelength range. This experimental system chooses the electron affinity group of 2,5-diaryl-1,3,4-oxadiazole that has good thermal stability, but generally has poor solubility in solvent [19]. In 1960s, Johnson synthesized aromatic polyethers containing 2,5-dipheny-1,3,4-oxadiazole [20], and discovered that using this aromatic ether as intervals not only increased the solubility of polymer but also obtained good thermal stability. Therefore in this research, 2,5-bis-(4-fluoroaryl)-1,3,4- oxadiazole was incorporated with 1-(1′-hydroxy-4′-phenylvinyl)-4-hydroxybenzene or 1-(1′-hydroxy-4′-naphthylvinyl)-4-hydroxybenzene to provide electron-transporting chromophores and emission chromophores.

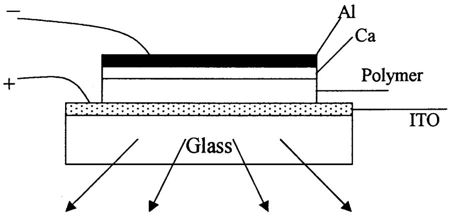
2. Experiment

2.1. Material and measurement

All reagents and solvents were reagent grade or were purified by standard methods before use. 4-fluorobenzoic acid, 4-fluoro-1-naphthoic acid, 4-methoxybenzaldehyde, 4-methoxy-1-naphthaldehyde, diethyl-4-methoxy- benzylphosphonate, potassium *tert*-butoxide and triethylene glycol from Lancaster Co. were used as received. *N*,*N*-dimethylformamide(DMF), *N*,*N*-dimethylacetamide(DMAC), *N*-methyl-2-pyrrolidone (NMP), *N*-cyclo-hexyl-2-pyrrolidone (CHP) and methanol from Acros Co. were used as solvent and purified before use.

Elemental analyses were performed by the Heraeus 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-TEMPII). A thermogravimetric analyzer (DuPont Model TGA 2950) was used to measure the weight loss of polymer films during the temperature scan from 30 to 600°C with the heating rate of 10°C/min in a stream of nitrogen. A differential scanning calorimeter (DuPont Model DSC 2010) was used to examine thermograms in the temperature range of 30–300°C with the heating rate 10°C/min. ^{1}H nuclear magnetic resonance (NMR) was performed in Acetone-d_6, CF_3COOD, or DMSO at 50°C. UV/Vis spectra were obtained with a Perkin–Elmer Lambda 40 spectrometer. Optical characterization was performed by photoluminescence (PL) measurement, where the 325 nm line of He–Cd laser with 20 mW power was used to excite the sample. Cyclic voltammetry (CV) was carried out in a one-compartment cell using a potentiostat/galvanostat (Model 610A from CH Instruments), with a unaqueous electrode (0.01 M $AgNO_3$, 0.1 M $(n\text{-Bu})_4NClO_4$/Acetonitrile) as the reference electrode, a Pt (1×3 cm^2) coated with a thin neutral polymer film to be tested as the working electrode, a blank platinum (Pt) strip as the counter electrode, and tetrabutylammonium perchlorate in dry acetonitrile (0.1 M) as electrolyte at a scan rate of 20 mV/s. Gel permeation chromatography with RI detector and column (PLgel 5 μm MIXED-D 300×7.5 mm from England Polymer Laboratories Ltd.) was used to measure molecular weight distributions (MWDs) relative to polystyrene standards at room temperature. The calibration curve was determined by use of six MW standards from 2930 to 3.77×10^5. The carrier solvent used was degassed NMP at a flow rate of 1 ml/min.

The OLED device consisting of a transparent electrode, a light-emitting polymer film, and a negative electrode, as shown in Scheme 1, was fabricated as follows. A solution was prepared under continuous stirring of polymer in solvent for 24 h in a beaker covered with aluminum foil. ITO glass with 20 Ω/cm^2 was cut into 2×2 cm^2 pieces and



Scheme 1.

then cleaned in an ultrasonic bath of isopropyl alcohol, methanol and acetone, respectively. A layer of about 150 nm thickness of polymer film was spin coated on ITO substrate. Calcium (Ca) and aluminum (Al) were deposited, respectively as cathode materials on the polymer film by evaporation technique under pressure of 10^{-6} Torr. The electroluminescence measurements have been carried out using Acton Research Corporation Spectra Pro 500.

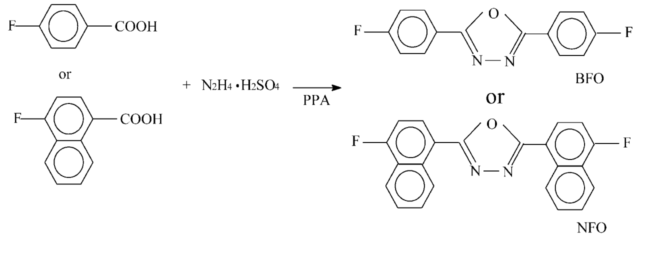
2.2. Synthesis of 2,5-bis(4-fluoroaryl)-1,3,4-oxadiazole (BFO and NFO)

2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole (BFO) was synthesized according to our previously published procedures [21] as shown in Scheme 1. The BFO was further recrystallized from methanol and dried. Yield 76%; mp 204–205°C.

2,5-Bis(4-fluoronaphthyl)-1,3,4-oxadiazole (NFO) was synthesized according to our previously published procedures [21] with some minor modifications. The NFO was further recrystallized from toluene and dried. Yield 70%; mp 232–233°C. The IR spectrum (KBr) exhibited absorption at 3066, 1675, 1598(–C=N–), 1493, 1429, 1160, 1093, 1070, 838, 763, 745 cm^{-1}. Anal. Calcd for $C_{22}H_{12}N_2OF_2$: C, 73.74; H, 3.35; O, 4.47; N, 7.82. Found: C, 73.78; H, 3.39; O, 4.38; N, 7.86. EIMS, *m/z*: 358(M$^+$). The synthetic scheme is shown in Scheme 2.

2.3. Synthesis of 1-(1′-methoxy-4′-arylvinyl)-4-methoxybenzene (MBBM and MBNM)

A 250 ml reaction vessel was equipped with a magnetic stirrer, reflux condenser, gas inlet and a rubber septum. It was charged with 6 mmol diethyl-4-methoxybenzylphosphonate, 7.8 mmol potassium *tert*-butoxide and 12 ml *N,N*-dimethylformamide (DMF). After stirring for 1 h at 5°C, the reaction mixture was slowly added to a solution of 6 mmol 4-methoxybenzaldehyde (or 4-methoxy-1-naphthaldehyde) in 6 ml DMF. After another 1 h stirring, the cooling bath is removed and the reaction mixture is allowed to warm up to room temperature and stirred for approximately 24 h. The mixture was precipitated into 500 ml of ice water. The yellow precipitate was recrystallized from methanol and dried.



Scheme 2.

1-(1′-Methoxy-4′-phenylvinyl)-4-methoxybenzene (MBBM), yield: 78%; the IR spectrum (KBr) exhibited absorption at 3011, 2964, 1584, 1520, 1504, 1463, 1386, 1301, 1264 (C–O–C), 1246, 1175, 1114, 1024 (C–O–C), 960 (C=C), 805, 763 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.98; H, 6.65; O, 13.33. Found: C, 79.91; H, 6.62; O, 13.30. EIMS, *m/z*: 240(M$^+$).

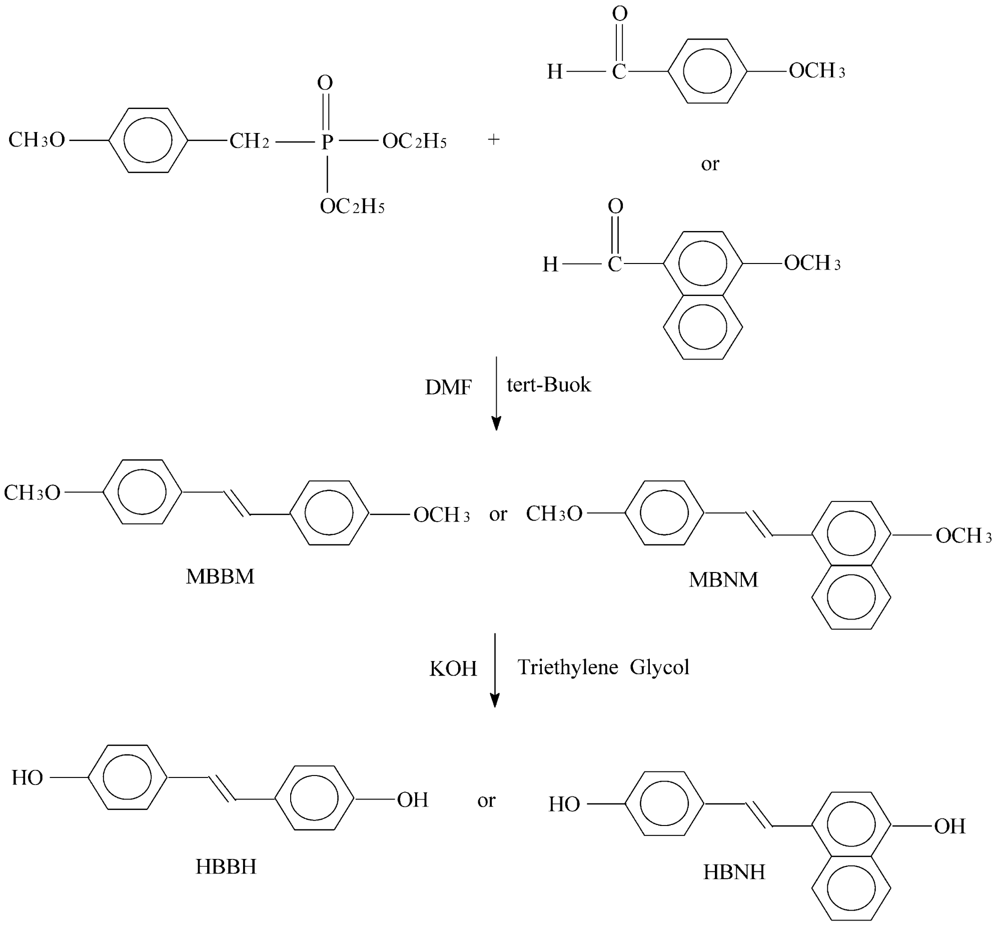
1-(1′-Methoxy-4′-naphthylvinyl)-4-methoxybenzene (MBNM), yield: 61%; the IR spectrum (KBr) exhibited absorption at 3009, 2965, 1584, 1504, 1458, 1386, 1301, 1264 (C–O–C), 1246, 1169, 1090, 1029 (C–O–C), 958 (C=C), 805, 763 cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.74; H, 6.22; O, 11.01. Found: C, 82.70; H, 6.20; O, 11.1. EIMS, *m/z*: 290(M$^+$). The synthetic scheme is shown in Scheme 3.

2.4. Synthesis of 1-(1′-hydroxy-4′-arylvinyl)-4-methoxybenzene (HBBH and HBNH)

4 mmol MBBM (or MBNM) is dissolved in a solution of potassium hydroxide in triethylene glycol (16 ml) and stirred for 24 h at 200°C. After completion of the reaction, the mixture was poured into 100 ml of deionized water. The mixture was first acidified and then was extracted 3–4 times with 150 ml of ethyl acetate. After evaporating the solvent, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (2:1 by volume) to give a yellow-brown oil. The collected product was recrystallized from chlorobenzene and dried to give the dihydroxy product. Yields of 1-(1′-hydroxy-4′-phenylvinyl)-4-hydroxybenzene (HBBH) and 1-(1′-hydroxy- 4′-naphthylvinyl)-4-hydroxybenzene (HBNH) were 68 and 45%, respectively. The synthetic scheme is shown in Scheme 3.

2.5. Synthesis of organic light emitting polymer

To a 200 ml reaction vessel equipped with a temperature controller, overhead stirrer and a Dean–Stark-trap was charged 1 mmol of respective monomers, 2.2 mmol K_2CO_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 toluene 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 another 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. Nevertheless, those comparison polymers containing



Scheme 3.

hexaethylene chain were synthesized with DMAC instead of NMP/CHP as solvent.

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 staring materials is outlined in Schemes 2 and 3. The structures of these products were characterized by IR, NMR and EA measurements and by DSC and TGA to analyze thermal properties of these polymers. The optical properties including absorption and luminescence of these polymers were measured with UV/Vis and PL systems and with cyclic voltammetry to measure reduction–oxidation potentials of these polymers.

3.1. Monomers synthesis and characterization

Two kinds of monomers were synthesized. 2,5-Bis(4-fluoroaryl)-1,3,4- oxadiazole (BFO or NFO) 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 polymers. The other advantage is that it can disperse negative charges in transition state when aromatic polyethers are synthesized, so the transition state would be stable and the reaction could be carried out more easily [22].

Fig. 1 shows that the ^{1}H NMR spectra of BFO and NFO. The hydrogens of aromatic ring neighboring with 1,3,4-oxadiazole are located at $\delta = 8.20$ and 9.05 ppm, respectively. If 1,3,4-oxadiazole is replaced by ketone group, the ^{1}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 to take place easily, the effect which will also happen in other systems of heterocyclic compounds, such as: triazoles, triazines,…etc.

In this study, the diarylethylene derivatives were used as emission chromophores in polymer. The syntheses of diarylethylene derivatives are performed according to Homer–Wadsworth–Emmons reaction and demethoxylation with strong base (Scheme 2). The strong acid, HI and HBr were widely used in the reaction of ether to alcohol [23]. But they also attack double bonds. Therefore, strong acids

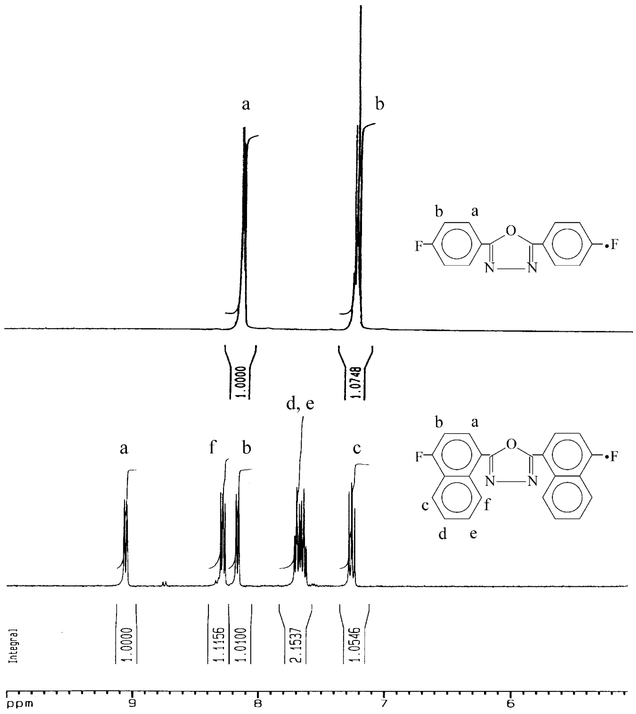


Fig. 1. ^{1}H NMR spectra of BFO (top) and NFO (bottom).

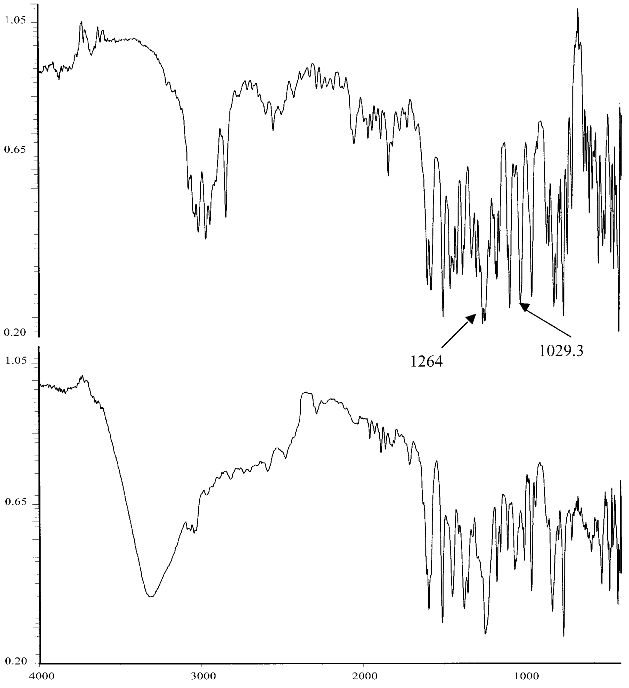


Fig. 3. FTIR spectra of MBNM (top) and HBNH (bottom).

such as HI and HBr are not adapted in this reaction system. Some Lewis acids like BBr_3 were also used due to the low reaction temperature. However, BBr_3 is not used because of instability in air and high toxicity. Although the complex, $BBr_3 \cdot S(CH_3)_2$, is stable in the air, it is not adapted because of low yield (8–11%) for HBNH monomer. The others, like pyridine hydrochloride yield only 10–15% and has apparent side reaction. The strong base (KOH) that was rarely used in the literature gave higher yield (40–50%) than those mentioned above.

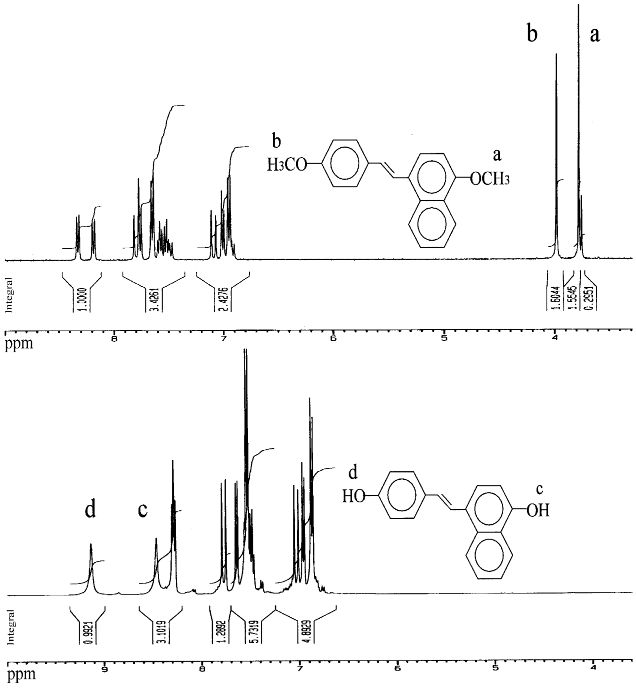


Fig. 2. ^{1}H NMR spectra of MBNM (top) and HBNH (bottom).

Fig. 2 shows the ^{1}H NMR spectra of MBNM (a) and the corresponding monomer HBNH (b). The chemical transformation is confirmed by the shifting of the peaks at 3.76 and 3.98 ppm, characteristic of methyl group, to the lower values of the field (8.46 and 9.13 ppm), characteristic of hydroxyl group. In the IR spectra of Fig. 3 (MBNM (a) and HBNH (b)), which also represents the transformation reaction, the absorption at 3306 cm^{-1} is due to hydroxyl group of HBNH, and the disappearance of the absorption at 1029 and 1264 cm^{-1} are due to symmetric and asymmetric stretching of aromatic ethers (C–O–C) of MBNM, respectively. The structures of MBBM and HBBH were confirmed by ^{1}H NMR spectra, elemental analysis, IR spectra and mass spectrometry, and were in good agreement with the proposed structures.

The photoluminescence spectra of the diarylethylene derivatives are shown in Fig. 4. The peak luminescent wavelengths are 386 and 434 nm for HBBH and HBNH, respectively. It is apparent that the naphthalene ring has shifted the wavelength more towards the red than benzene ring due to its conjugated phenomenon. The result is in agreement with our expectation that the spectrum of HBNH should emit light in the blue emission region. Therefore, the diarylethylene derivatives can be adapted as the precursors for organic light emitting materials.

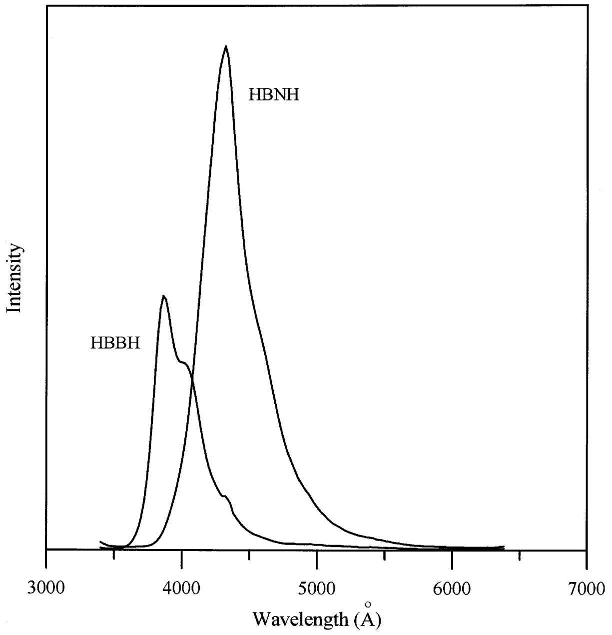


Fig. 4. The photoluminescent spectra of the diarylethylene derivatives.

3.2. Synthesis of organic light emitting polymer and characterization

In order to understand the physical and optical properties of the synthesized polymers, four kinds of polymers, P1–P4 were synthesized. The effects of the extended rings, benzene and naphthalene on the luminescent properties were studied. This study also synthesized the P5 and P6, which contain six-methylene groups in the main chain. The comparison of P5–P6 with Pl–P4 that contain the electron-transporting chromophore will reveal the effect of the electronic affinities of these polymers. Polymers were synthesized according to our previously published procedures [21] as shown in Scheme 4. The reaction conditions and results are listed in Table 1. The M_ws are in the order of 10^4 (relative to the molecular weight standards of polystyrene), which is sufficiently high to be considered as a polymer. The transparent films can be obtained by spin coating of the polymer solution. From the IR spectrum which corresponds to polyether P5, the absorption bands situated at 1265 and 1025 cm^{-1} (C–O–C, stretch) are characteristic of the new formed etheric linkage and at 2933 and 2853 cm^{-1} (sat. C–H stretch) are characteristic of aliphatic C–H group. The solubilities of polymers in various solvents are listed in Table 2. Due to the introduction of aliphatic long chain segments into the polymer, P5 and P6 have exhibited an excellent solubility toward test solvents.

Table 2
Solubilities of polymers ((+ +) Soluble at room Temperature; (±) Partially soluble on heating; (− −) Insoluble)

Sample	DMSO	DMAC	NMP	Pyridine	$CHCl_3$	THF	Toluene
E_T (30)[a]	45.1	43.7	42.2	40.5	39.1	37.4	33.9
P1	−−	++	++	++	±	±	−−
P2	−−	++	++	++	−−	−−	−−
P3	−−	±	++	±	−−	−−	−−
P4	−−	−−	++	±	−−	−−	−−
P5	−−	±	++	±	±	±	−−
P6	−−	±	++	±	±	−−	−−

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

3.3. Thermal analysis of polymer

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 operating temperature is high. If the polymer crystallizes, it may separate in phases and will reduce the device efficiency.

DSC and TGA are the most favored techniques for rapid evaluation in comparing and ranking the thermal stability of various polymers. Table 3 shows polymers with 1,3,4-oxadiazole ring having T_gs in the range of 213–241°C and

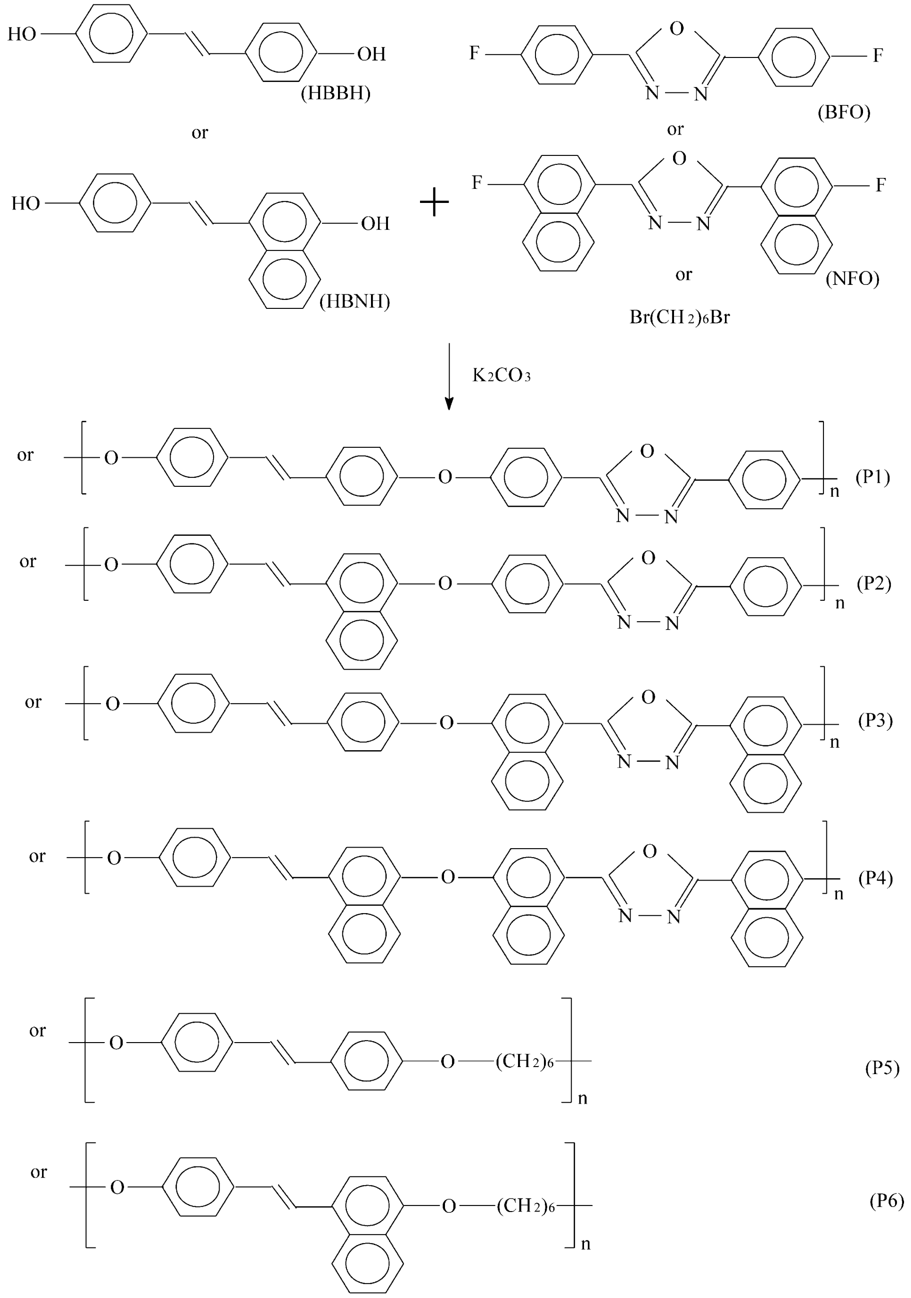
Table 1
Polymerization conditions and results of polymers P1–P6

Items	P1	P2	P3	P4	P5	P6
Reaction temperature (°C)	170	180	170	180	160	160
Reaction time (h)	12	24	12	24	24	24
Solvent	NMP/CHP	NMP/CHP	NMP/CHP	NMP/CHP	DMAc	DMAc
Yield (%)	79	72	62	54	64	59
Calcd[a]	$C_{28}H_{18}N_2O_3$	$C_{32}H_{20}N_2O_3$	$C_{36}H_{22}N_2O_3$	$C_{40}H_{24}N_2O_3$	$C_{20}H_{22}O_2$	$C_{24}H_{24}O_2$
Found[b]	$C_{28.4}H_{17.8}N_{1.9}O_x$	$C_{32.1}H_{22.6}N_2O_x$	$C_{35.8}H_{23.1}N_{2.1}O_x$	$C_{41.2}H_{23.7}N_{1.9}O_x$	$C_{21.1}H_{22.6}O_x$	$C_{24.7}H_{22.8}O_x$
Intrinsic Viscosity (dl/g)	0.59	0.54	0.49	0.42	0.47	0.46
$10^{-4}M_w$	3.9	3.7	3.3	3.1	3.2	3.3
$10^{-4}M_n$	1.8	1.6	1.2	1.1	1.7	1.6
PD[c]	2.2	2.3	2.7	2.8	1.9	2.1

[a] Molecular formula of repeating unit.

[b] Molecular formula of repeating unit was characterized by EA measurements.

[c] PD: M_w/M_n.



Scheme 4.

Table 3
Thermal properties of polymers

NO.	T_g[a] (°C)	T_m[a] (°C)	Td[b] (°C)
P1	215	–	473
P2	213	–	480
P3	238	–	482
P4	241	–	490
P5	76	176	387
P6	78	181	402

[a] Determined by DSC at a heating rate of 20°C/min.

[b] Temperature at which 5% weight loss was recorded by means of TGA at heating rate of 20°C/min.

no T_m peak even after the temperature went above 330°C. The T_gs of these polymer with 1,3,4-oxadiazole are much higher than P5 and P6 with long aliphatic chain in polymer. Due to the replacement of long aliphatic chain with the rigid 1,3,4-oxadiazole groups, the rotation of polymer chain became difficult. Moreover, much rigid naphthalene groups on main chain of P4 have obstructed the rotation of the polymer chain. Therefore, the T_g of the P4 (241°C) is higher than P5 (76°C) or P6 (78°C). Another phenomenon that is observed is that polymers containing six methylene groups crystallize easily, so P5 and P6 are found to have T_m at 176 and 181°C, respectively. The main factors that affect the T_g

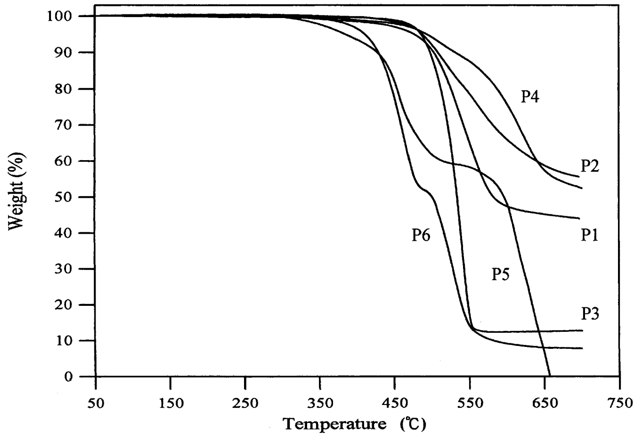


Fig. 5. TGA thermograms of P1–P6.

and T_m are: (1) the rigid group in polymer chain; (2) the polar group; (3) the form and size of side chain.

From the results of TGA as shown in Fig. 5 and Table 3, it is apparent that these polymers have excellent thermal stability. The starting temperatures of degradation are all higher than 470°C for P1–P4. For P5 and P6, a drastic weight decrease was observed when the temperature was close to 400°C, and another drastic decrease near 470°C. The first weight loss maybe due to the degradation of the aliphatic chain, and near 470°C it is due to the degradation of the emission chromophores. As expected poly(arylether) containing 1,3,4-oxadiazole will have higher thermal stability than that of P5 and P6 containing the aliphatic chain.

3.4. Optical properties

The emitting wavelengths of the electroluminescent polymers are dependent on the structure of polymers. The absorption and PL spectra were measured. Figs. 6 and 7 show the UV/Vis absorption spectra of polymer solution and thin film, respectively. The peak absorption wavelengths are shown in Table 4. From Table 4, it is found that the polymer solution has apparently shifted 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. [24]. 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 5 shows the UV/Vis absorption peak values for 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 a highly polar solvent produced the orientation polarization effect and generated an electrical field with emission chromophores. The electrical field has changed the basic state of molecules. In Ref. [25], a similar phenomenon was discussed but the shift was only a few nanometers in this

Table 4
The absorption and photoluminescent maximums of P1–P6 in film or solution at room temperature

NO.	UV (solvent) (nm)	UV (film) (nm)	PL (film) (nm)	Stokes shift[a] (nm)
P1	298 (Chloroform)	311	377	66
P2	307 (NMP)	316	425	109
P3	320 (NMP)	325	405	80
P4	334 (NMP)	358	456	98
P5	331 (Chloroform)	336	394	58
P6	357 (Chloroform)	369	443	74

[a] Stokes shift = PL (film) (nm) − UV (film) (nm).

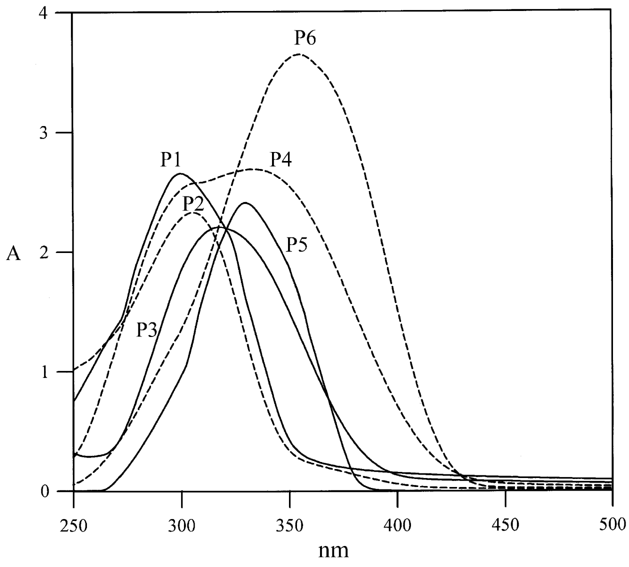


Fig. 6. UV/Vis absorption spectra of P1–P6 in the solution state.

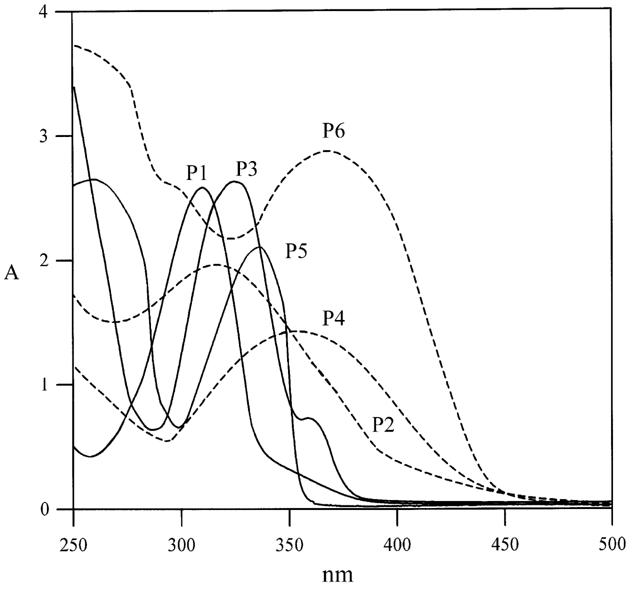


Fig. 7. UV/Vis absorption spectra of P1–P6 as thin films.

Table 5
UV/Vis absorptions of P1, P5 and P6 in various polar solvents at room temperature [(– –) insoluble]

	λ max.(nm) in Toluene	THF	$CHCl_3$	Pyridine	NMP	DMAC
Solvent polarity	Low					High
P1	– –	295	298	304	302	298
P5	– –	325	331	336	332	328
P6	– –	– –	357	360	362	355

study. It is mainly due to the absence of strong donor–acceptor pairs in the emission chromophores. Although the oxygen atoms have the unshared electron pairs, they are not strong donors. Another reason is that the polymer is not as easily surrounded by solvents as small molecules are. These reasons made the absorption spectra less shifted.

The photoluminescent spectra of polymers are shown in Fig. 8. The luminescent peak wavelengths shifted to the longer wavelength with increasing conjugating rings. The peak wavelengths are shown in Table 4. It is found that these polymers (P2, P4 and P6) have three conjugating rings, the PL peak was longer than those (P1, P3 and P5) by few nanometers, since the conjugation effect from the naphthalene ring is much stronger than that of the benzene ring and thus the conjugation length is increased. All the polymers almost 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 4, 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 P2 and P4, they are the best polymers evaluated in this study for OLEDs.

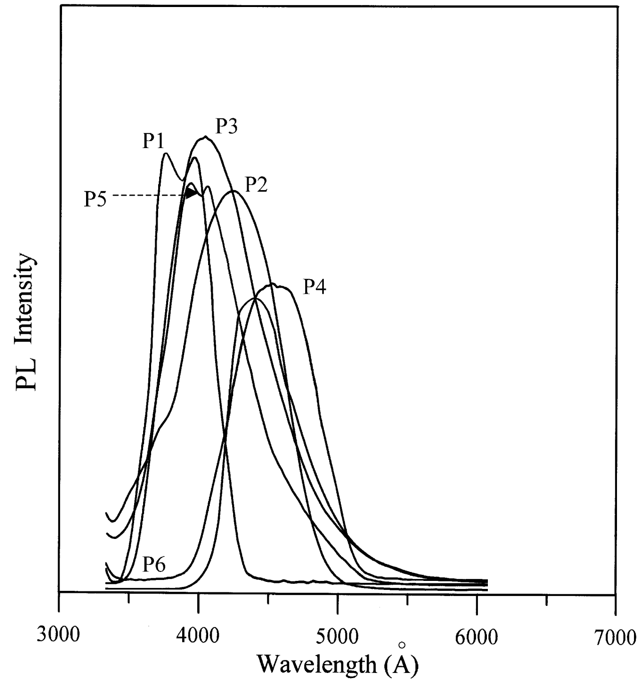


Fig. 8. The photoluminescent spectra of the polymers.

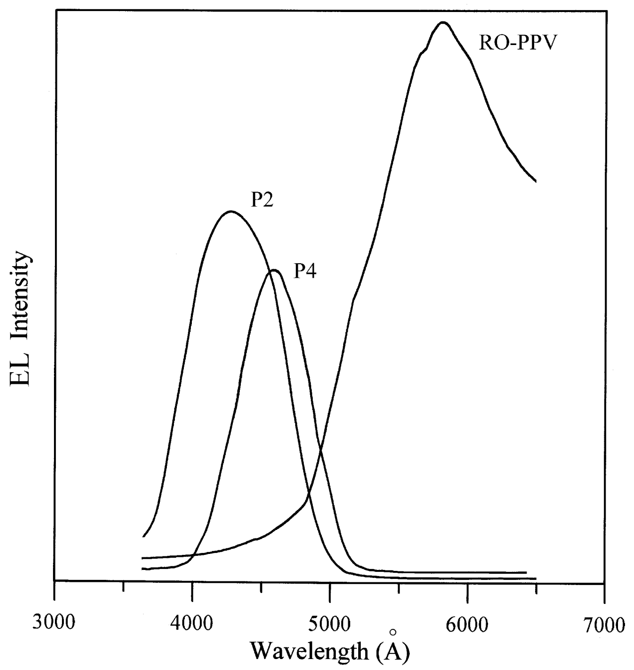


Fig. 9. The electroluminescent spectra of the devices fabricated using P2, P4, and RO-PPV.

Fig. 9 shows the electroluminescent (EL) spectra of the devices using P2, P4, and RO-PPV. The spectra of the devices using P2 and P4 are in good agreement with their PL spectra shown in Fig. 8. The EL intensity of the devices using our novel polymers were slightly lower than commercialized RO-PPV (Poly(2-methoxy-5(2′-ethylhexylexy)-*p*-phenylene vinylene) made by Sumitomo Chemical Co. Ltd. The effect of conjugation length on the charge transport and energy band structure, the temperature dependence of EL and quantum efficiency of the device fabricated using our novel polymers will be discussed in the future.

Table 6
Electrochemical data for P1–P6 obtained by cyclic voltammetry. (The measuring condition is at room temperature under nitrogen atmosphere. Working electrode is platinum disc electrode. Reference electrode is Ag/Ag^+ (0.01 M $AgNO_3$, 0.1 M (n-Bu)$_4$NClO$_4$/ Acetonitrile) electrode. Auxiliary electrode is platinum wire electrode. Supporting electrolyte is (n-Bu)$_4$NClO$_4$ in Acetonitrile)

No.	$V^1_{red.}$ (V)	$V^2_{red.}$ (V)	$V^1_{ox.}$ (V)	$V^2_{ox.}$ (V)
P1	−1.424	−1.911	0.117	−1.613
P2	−1.531	−1.812	0.063	−1.546
P3	−1.392	−1.784	0.108	−1.586
P4	−1.437	−1.685	−0.021	−1.530
P5	−1.411	–	0.110	–
P6	−1.529	–	−0.063	–

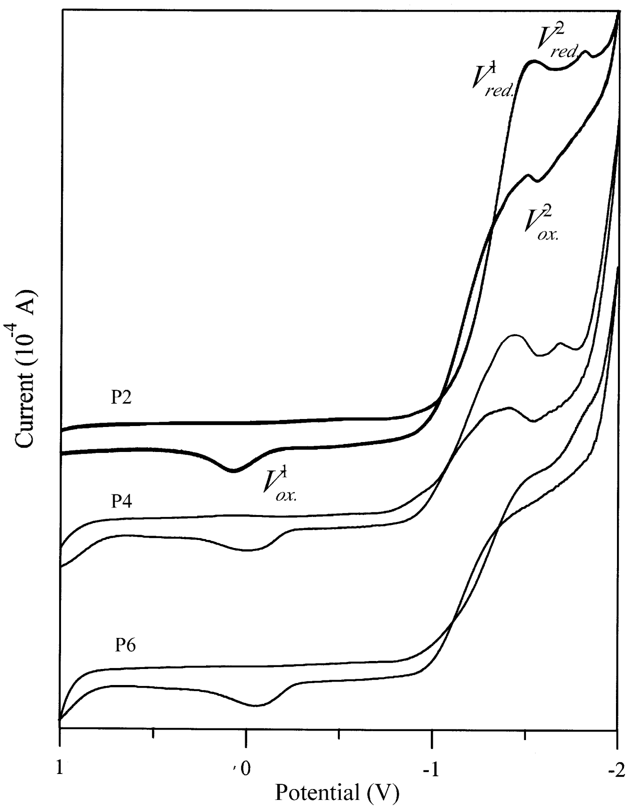


Fig. 10. Cyclic voltammogram of P2, P4, and P6 in film on Pt electrode in CH_3CN solution of $(n\text{-Bu})_4NClO_4$ (0.1 M) at a scanning rate of 100 mV/s.

CV provides the technique in evaluating the electron affinity effect of the polymer with 1,3,4-oxadiazole ring. The technique evaluates the electron affinity and reduction potential by scanning toward negative voltage; it also evaluates the hole affinity by scanning toward positive voltage. The CV spectra of P2, P4, and P6 are shown in Fig. 10. The oxidation–reduction potential are shown in Table 6. It was found that P1 (−1.613, −1.911 V) and P3 (−1.586, −1.784 V) have one more set of oxidation–reduction potential than P5; P2 (−1.546, −1.812 V) and P4 (−1.530, −1.685 V) also have one more set of oxidation–reduction potential than P6. This is attributed to the presence of 1,3,4-oxadiazole structure. Due to the naphthalene ring, P3 and P4 are more stable than P1 and P2 in conjugation; the oxidation–reduction for P3 and P4 are easier than that for P1 and P2 and the result was shown in Table 6. The oxidation–reduction potential of P3 and P4 are lower than P1 and P2. Therefore, P3 and P4 are more capable of accepting electrons and holes than P1 and P2.

4. Conclusion

Several novel diarylethylene-containing emission chromophores were synthesized and incorporated within electron transporting chromophores. The physical properties of polymers were successfully modified by the incorporation of 1,3,4-oxadiazole ring and using moldability of aromatic ether as an interval, so they generally exhibited better solubility and greater thermal stability. Moreover, the effects of structures on optoelectric properties were investigated. All the resulting polymers containing oxadiazole group were thermally stable below 470°C. The absorption peaks of these polymers varied from 310 to 370 nm, while the photoluminescent peaks varied from 377 to 456 nm. The luminescent wavelength of P4 with naphthalene ring shifted 79 nm towards red relative to P1. It is attributed to the fact that the conjugation effect from benzene is much less than that from naphthalene. By comparing the oxidation–reduction potential measured by CV, P1–P4 with 1,3,4-oxadiazole rings have one more oxidation–reduction peak than P5 and P6 which indicates that they are more capable of accepting electrons in our expectation.

Acknowledgements

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References

[1] Wessling RAJ. Polym Sci Polym Symp 1986;72:55.
[2] Tang CW, VanSlyke SA. Appl Phys Lett 1987;51:913.
[3] Pope M, Kallmann H, Magnante PJ. Chem Phys 1963;38:2024.
[4] Marder SR, Sohn JE, Stucky GD, editors. Materials for nonlinear optics; chemical perspectives. Washington, DC: ACS, 1991.
[5] Bredas JL, Chance RR, editors. Conjugated polymeric materials: opportunities in electronics, optoelectronics, and molecular electronics. Dordrecht: Kluwer, 1990.
[6] Miller JS. Adv Mater 1993;5:587 see also p. 671.
[7] Burrououghes JH, Bradley DDC, Brown AR, Marks RN, MacKay K, Friend RH, Burn PL, Holmes AB. Nature 1990;347:539.
[8] Grem G, Leditzky G, Leising G. Adv Mater 1992;4:36.
[9] Grem G, Leising G. Synth Met 1993;55:4105.
[10] Ohmori Y, Uchida M, Muro K, Morishima C, Yoshino K. Mol Cryst Liq Cryst 1993;227:285.
[11] Kraft A, Grimsdale AC, Holmes AB. Angew Chem Int Ed Engl 1998;37:402.
[12] Gustafsson G, Cao Y, Treacy GM, Klavetter F, Colaneri N, Heeger AJ. Nature 1992;357:477.
[13] Gmeiner J, Karg S, Meier M, Rie W, Strohriegl P, Schwoerer M. Acta Polym 1993;44:201.
[14] Benjamin I, Faraggi EZ, Cohen G. Synth Met 1997;84:401.
[15] Yang Z, Sokolik I, Karasz FE. Macromolecules 1993;26:1188.
[16] Brown AR, Brdaley DDC, Burroughes JH, Friend RH, Greenham NC, Burn PL, Holmes AB, Kraft A. Appl Phys Lett 1992;61: 2793.
[17] Strukelj M, Papadimitrakopoulos F, Miller TM, Rothberg LJ. Science 1995;267:1969.
[18] Yang Y, Pei QJ. Appl Phys 1995;77:4807.
[19] Bao Z, Peng Z, Galvin ME, Chandross EA. Chem Mater 1998;10: 1201.
[20] Johnson RN, FarnHam AG, Clendinning RA, Hale WF, Merriam CN. J Polym Sci Part A-1 1982;5:2375.
[21] Sun YM, Wang CS. Polymer 2001;42:1035.
[22] Hedrick JL. Polym Bull 1991;25:543.
[23] Bhatt MV, Kulkarni SU. Synthesis 1983;4:249.
[24] Geerts Y, Keller U, Scherf U, Schneider M, Mullen K. Polym Prepr 1984;38:315.
[25] Reichardt C. Solvents and solvent effects in organic chemistry. New York: Weinheim, 1988. p. 359.