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Synthesis of Poly(*p*-phenylene-vinylene) Derivatives Containing an Oxadiazole Pendant Group and Their Applications to Organic Electronic Devices

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Poly(*p*-phenylene vinylene) (PPV) derivatives with 2,5-diphenyl-1,3,4-oxadiazole-diyl (OXD) as the side chain, poly[2-{4-[5-(4-(heptyloxy)phenyl)-1,3,4-oxadiazole-2-yl]phenyl-oxy}-1,4-phenylene-vinylene] (OXH-PPV), poly[2-{4-[5-(4-(heptyloxy)phenyl)-1,3,4-oxadiazole-2-yl]phenyl-oxy}-1,4-phenylene-vinylene-*co*-2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (OXH-PPV-*co*-MEH-PPV), and poly[2-methoxy-5-(2'-ethylhexyl-oxy)-*p*-phenylene vinylene] (MEH-PPV), were synthesized via a modified Gilch route. The electron-deficient oxadiazole motive was introduced on the side chain of the polymer backbone to increase the electron-affinity of the polymers. The electroluminescent (EL) properties of the resulting polymers as an active layer, were investigated by the fabrication of single-layer LEDs and the devices using OXH-PPV-*co*-MEH-PPV showed better EL properties than those using pure MEH-PPV. Also, to investigate the switching properties of the resulting polymers as an active layer, OFET devices were fabricated in a top-contact/bottom-gate configuration. The resulting FETs exhibited typical *p*-channel characteristics, field-effect mobility of 6.5×10^{-4} – 7.0×10^{-5} cm² V⁻¹ s⁻¹, and on-off ratio of about 10^4 – 10^5 .

Keywords: Poly(p-phenylene vinylene) (PPV) Derivatives, Oxadiazole, OLED, OTFT.

1. INTRODUCTION

The interest for fusing organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs) to produce organic light-emitting FETs (OLEFETs) has been increasing and those demands aim to achieve simplified organic active matrix displays.¹ To achieve efficient OLEFETs, it is necessary to prepare adequate organic materials with both efficient electroluminescence and transistor characteristics. However, it is still difficult to find ideal candidates from well-established OLED materials, since most OLED active materials have no high performance FET characteristics probably due to their amorphous morphologies. Moreover, the recent progress in OFETs has revealed that highly packed molecular thin films with tight intermolecular π stacking have demonstrated pronouncedly high carrier mobilities exceeding

 $\sim 1~{\rm cm}^2~{\rm V}^{-1}~{\rm s}^{-1.2}$ Instead of having a high performance TFT function, however, most TFT active materials demonstrate rather weak photoluminescence (PL) due to their strong molecular packing, i.e., concentration quenching, which means that they are difficult to use in light-emitting applications. In unipolar light-emitting transistors, light emission is restricted to a region very close to the contact that injects the charge carriers having lower mobility.^{3–10}

In contrast, an ambipolar light emitting transistor would allow the electron-hole balance as well as the location of the recombination zone between source and drain electrode to be tuned by the gate voltage, hence improving the quantum efficiency.^{11–18} Therefore, we need to satisfy the demand and find organic materials that provide both light-emitting and ambipolar transistor characteristics. An efficient OLEFET device, as mentioned above, requires balanced injection and transport of both electrons and holes.¹⁹ However, most of the conjugated polymers developed so far transport electrons much less efficiently

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than holes,²⁰ which significantly decrease the efficiency of the device. For improving the luminance efficiency, many research groups have introduced electron transport moieties on the side chain of the polymer backbones or polymer main chains.^{21–26} These polymers showed enhanced electron injection and improved balance in carrier mobility. One of the most widely used electron transport moieties is aromatic 1,3,4-oxadiazole-based compounds with high electron affinities.²⁷

For those purposes, in this paper, PPV derivatives both homopolymers and their corresponding copolymers were synthesized. The design is based on the consideration that the PPV backbone is a good hole-transporting electroluminescent material, the electron-deficient moiety, 2,5diphenyl-1,3,4-oxadiazole-diyl (OXD), as the side chain, provides a highly improved electron-transporting property due to interchain interaction and efficient mixing between OXD moieties with chromophores on the main chains, and the linear alkoxy side group next to OXD unit provides solubility and helps crystalline packing. Also, electrooptical properties and device performance could be easily controlled by adjusting the feed ratio of the OXD content through copolymerization.

2. EXPERIMENTAL DETAILS

2.1. Materials

Chemicals and solvents were reagents grades and purchased from commercial sources (mostly from Sigma-Aldrich Co.). THF were distilled to keep them anhydrous before use. The other chemicals were used without further purification. All reactions were carried out under a nitrogen atmosphere. Column chromatography was performed using silica gel (Merck, 230–400 mesh).

2.2. Characterization and Measurements

¹H NMR spectra data were obtained from a JEOL JNM-LA300WB 300 MHz spectrometer with TMS as the internal reference. Differential scanning calorimetry (DSC; TA-2010) was conducted under a nitrogen atmosphere at a heating rate of 10 °C/min. Samples were scanned from 40 °C to the decomposition temperature. T_d was measured at a temperature of 5% weight loss for the polymer. Thermo-gravimetric analysis (TGA; TA-2050) was also performed under a nitrogen atmosphere. The UV/Visible Spectra of the polymers were measured using a UV/Visible Spectrophotometer (HP 8453). Photoluminescence (PL) spectra of the polymers were obtained using an ACTON spectrometer connected to a photo-multiplier tube (Acton Research Co. SpectraPro-300i) with a xenon lamp as the excitation source.

Electrochemical measurements of the polymers were performed using cyclic voltametry (CV) at room temperature in a three-electrodes cell with Pt wire as the counter electrode and Ag wire as the reference electrode immersed in a 0.1 M solution of tetrabutylammonium-perchlorate (Bu_4NCl_4) in acetonitrile solution as the electrolyte. The molecular weight and polydispersity of the polymers in THF solution were determined by gel permeation chromatography (GPC, Futecs, NS2001).

2.3. Synthesis

2.3.1. Synthesis of 4-Fluoro-Benzohydrazide, 1

In a 250 mL three-neck flask, hydrazine monohydrate (35.04 g, 700 mmol) was dissolved under nitrogen in 40 mL of ethanol. Ethyl-4-fluorobenzoate (16.81 g, 100 mmol) was added dropwise. The reaction mixture was refluxed for 5 hrs. Upon completion, the reaction mixture was recrystallized from methanol. A white crystal solid, 4-fluoro-benzohydrazide, 1 was obtained (12.80 g, 83%). ¹H NMR (300 MHz, DMSO-d₆): δ 4.46 (*s*, 2 H, NH₂), 7.25 (*t*, 2 H, *J* = 8.8 Hz, aromatic protons), 7.85 (*dd*, 2 H, *J* = 5.5, 8.8 Hz, aromatic protons), 9.77 (*s*, 1 H, NH).

2.3.2. Synthesis of (4-heptyl)Oxybenzoyl-4-Fluoro-Benzohydrazide, 2

In a 250 mL three-neck flask equipped with a nitrogen inlet, 4-fluoro-benzohydrazide, 1 (5.86 g, 38 mmol) and triethylamine (6.07 g, 60 mmol) were dissolved in 200 mL of dichloromethane. 4-heptyloxy-benzoyl chloride (11.70 g, 46 mmol) was added at a rate of 20 mL/h via a syringe pump. The reaction mixture was then heated to reflux for 1.5 hrs. After confirmation of the disappearance of 4-fluoro-benzohydrazide, 1, by TLC, the mixture was cooled to room temperature, and then the reaction was diluted with dichloromethane followed by extraction with water and HCl (aq). The dichloromethane solution was dried over MgSO₄, and the dichloromethane was removed under reduced pressure. The crude product was purified by flash chromatography (hexane/ethyl acetate (8:2), silica gel) and recrystallized from dichloromethane/methanol yielding (4-heptyl)-oxybenzoyl-4-fluoro-benzohydrazide, 2 (12.21 g, 86%). ¹H NMR (300 MHz, CDCl₃): δ 0.88 $(t, J = 6.0 \text{ Hz}, 3 \text{ H}, \text{CH}_3), 1.30-1.80 (m, 10 \text{ H}, 5\text{CH}_2),$ $3.95 (t, J = 6.0 \text{ Hz}, 2 \text{ H}, \text{ OCH}_2), 6.82-6,85, 7.0-7.04,$ 7.77–7.87 (m, 8 H, aromatic protons), 9.71, 10.12 (s, s, 2 H, NH).

2.3.3. Synthesis of 2-{(heptyloxy)-phenyl}-5-(4-fluoro-phenyl)-1,3,4-Oxadiazole, 3

In a 250 mL three-neck flask, (4-heptyl)oxybenzoyl-4fluoro-benzohydrazide, 2 (2.64 g, 7.1 mmol), and thionyl chloride (4.22 g, 35.5 mmol) were dissolved in 100 mL of benzene. The mixture was stirred under nitrogen and brought to reflux for 4 hrs. After confirmation of the disappearance of (4-heptyl)oxybenzoyl-4-fluorobenzohydrazide, 2, by TLC, the mixture was cooled to

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room temperature, poured into excess water, and extracted with ether. The combined organic layers were washed several times further with water, dried over anhydrous MgSO₄, and filtered. The ether was removed by evaporation under reduced pressure. It was recrystallized from dichloromethane/methanol to give 2.07 g (82%) of pure product. ¹H NMR (300 MH_Z, CDCl₃): δ 0.89 (*t*, *J* = 6.0 Hz, 3 H, CH₃), 1.32, 1.81 (*m*, 10 H, 5CH₂), 4.03 (*t*, *J* = 6.0 Hz, 2 H, OCH₂), 7.03, 7.21, 8.02, 8.10 (*m*, 8 H, aromatic protons).

2.3.4. Synthesis of 2-{(heptyloxy)phenyl}-5-(4-(2,5dimethylphenoxy)phenyl)-1,3,4-Oxadia-Zole, 4

In a 250 mL three-neck flask equipped with a nitrogen inlet, 2-{(heptyloxy)-phenyl}-5-(4-fluoro-phenyl)-1,3,4-oxadiazole, 3 (2.02 g, 5.7 mmol) and 2,5-dimethylphenol (2.09 g, 17.1 mmol) were dissolved in 80 mL of DMF. After addition of potassium tert-butoxide (1.92 g, 17.1 mmol), the reaction mixture was refluxed for 4 h. After confirmation of the disappearance of 2-{(heptyloxy)-phenyl}-5-(4-fluorophenyl)-1,3,4-oxadiazole, 3, by TLC, the mixture was cooled to room temperature, poured into excess water, and extracted with ether. The organic phase was washed neutrally, dried (MgSO₄) and evaporated to dryness. The product was recrystallized from methanol and washed several times with hexane to give white crystals of 2-{(heptyloxy)phenyl}-5-(4-(2,5-dimethylphenoxy)phenyl)-1,3,40xadiazole, 4 (1.88 g, 72.5%). ¹H NMR (300 MHz, CDCl₃): δ 0.88 (t, J = 6.0 Hz, 3 H, CH₃), 1.31, 1.77 (m, 10 H, 5CH₂), 2.15, 2.31 (s, s, 6 H, 2CH₃ on aromatic ring), 4.01 (t, J = 6.0 Hz, 2 H, OCH₂), 6.81, 7.00, 7.13, 8.03 (m, 11 H, aromatic protons).

2.3.5. Synthesis of 2-{4-[2,5-Bis(bromomethyl) phenoxy]phenyl-5-{4-[heptyloxy]phenyl}-1,3,4-Oxadiazole, 5

A mixture of 1.87 g of 2-{(heptyloxy)phenyl}-5-(4-(2,5dimethylphenoxy)phenyl)-1,3,4-oxadiazole, 4 (4.1mmol) and 2.04 g of N-bromo-succinimide (NBS) (11.48 mmol) was dissolved in 70 mL of benzene. A catalytic amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed for 4 hrs under a nitrogen atmosphere. The completion of the reaction was indicated by the appearance of succinimide on the surface of the reaction solution. A solution was obtained after filtration of the succinimide. The solution was then poured into water and extracted with dichloromethane. The organic layer was collected and dried using MgSO₄, and the solvent was removed by evaporation under reduced pressure. The crude product was purified by column chromatography (hexane/ethyl acetate (9.5:0.5), silica gel) affording 0.97 g (39%) of a slightly yellowish powder. ¹H NMR (300 MHz, CDCl₃): δ 0.89 (t, J = 6.0 Hz, 3 H, CH₃), 1.32, 1.81 $(m, 10 \text{ H}, 5\text{CH}_2), 4.03 (t, J = 6.0 \text{ Hz}, 2 \text{ H}, \text{OCH}_2), 4.39,$

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4.54 (*s*, *s*, 4 H, 2CH₂Br on aromatic ring), 6.99, 7.16, 7.44, 8.03–8.14 (*m*, 11 H, aromatic protons).

2.3.6. Synthesis of Poly[2-{4-[5-(4-(heptyloxy)phenyl)-1,3,4-oxadiazole-2-yl]phenyl-oxy}-1,4-phenylene vinylene] (OXH-PPV)

To a 100 mL Schlenk flask dried with stream of hot air and flushed with nitrogen, 2-{4-[2,5-bis(bromomethyl) phenoxy]phenyl-5-{4-[heptyloxy]phenyl}-1,3,4-oxadiazole, 5 (0.306 g, 0.5 mmol) and 4-methoxy-phenol (1.24 mg, 2.0 mol%) were added and then it was dried and flushed with nitrogen again, and dissolved in 15 mL of dry THF. A solution of t-BuOK in THF (2.5 mL, 1.0 M) was then added at a rate of 20 mL/h via a syringe pump. After the complete addition of the base, the reaction mixture was stirred at room temperature for 1 hr. The color of the reaction mixture changed from colorless to yellowish, then to orange, and also the viscosity increased. The reaction mixture was poured into rapidly stirred 200 mL of methanol to precipitate the polymer. The collected polymer was Soxhlet-extracted with MeOH, Acetone, Hexane, MC and chloroform. The resulting polymer was redissolved in chloroform and reprecipitated in MeOH. After filtration and drying under vacuum, a bright yelloworange polymer was obtained (0.144 g, 64%). ¹H NMR (300 MHz, CDCl₃): δ 0.90 (br, 3 H, CH₃), 1.26, 1.79 (br, 10 H, 5CH₂), 4.01 (br, 2 H, -OCH₂), 6.99, 8.02 (br, 11 H, aromatic protons and vinylic protons).

Poly[2-{4-[5-(4-(heptyloxy)phenyl)-1,3, 4-oxadia-zole-2-yl] phenyl-oxy}-1,4-phenylenevinylene-*co*-2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (OXH-PPV-*co*-MEH-PPV) were prepared by varying the amount of monomers 5 and α, α' -Dibromo-2-methoxy-5-(2-ethylhexyl-oxy)xylene (for MEH-PPV) in the feed and following the similar procedure described for OXH-PPV.

2.4. Fabrication of EL Devices

The OLED devices had the configuration ITO/PEDOT:PSS (30 nm)/polymer (70 nm)/Al (150 nm). The thickness of all organic layers was determined by surface profiler (ET3000i, Kosaka Laboratory Ltd.). The OLED devices were fabricated on the glass substrate, pre-coated with indium-tin-oxide (ITO), which was cleaned in an ultrasonic bath with acetone, detergent, deionized water, and iso-propanol and surface treatment was performed by UVozone before use. The hole injecting poly(3,4-ethylene dioxythiphene) (PEDOT) were spin-coated on the ITO with a thickness of 30 nm. PEDOT was baked at 120 °C for 5 min under N₂. Then a layer of emitting polymers were spin-coated from chlorobenzene solution (1 wt%) and baked at 150 °C for 30 min under N2. Finally, a Al metal electrode was deposited by thermal evaporation at a pressure of 10^{-5} Torr through a shadow mask. The pixel size was 4 mm^2 .

2.5. Fabrication of EL Devices

The OTFT devices were fabricated in a top-contact/ bottom-gate configuration. The commercially available 300 nm thick SiO₂/Si (n+) wafer was used as a substrate after cleaning with acetone, iso-propanol, and deionized water. The surface of SiO₂/Si substrate was treated with hexamethyldisilane to form a hydrophobic monolayer surface. Then, polymers 6c-6e were spin coated from 0.5 wt% solution in chlorobenzene with a thickness of about 60–80 nm. The spin-coated films were annealed at 110 °C for 30 min in N₂-purged glove box. Finally, gold (50 nm) electrode was thermally vapor deposited. A shadow mask was used to define the source and drain electrodes. The channel width and length were 1.5 mm and 50 μ m, respectively. All the measurements were carried out in an N₂-purged glove box.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

Figure 1 shows the synthetic route for the 1,3,4-oxadiazole containing monomer, corresponding homopolymer, and their copolymers with various compositions of MEH-PPV. The synthetic routes were a little bit complicated, but all of the intermediate compounds were obtained with high yields.

In the first step, 4-fluoro-benzohydrazide, 1, was synthesized by the reaction of ethyl-4-fluorobenzoate with hydrazine monohydrate to give the hydrazide. Condensation of hydrazide, 1, with 4-heptyloxy-benzoyl chloride (4-heptyl)oxybenzoyl-4-fluoro-benzohydrazide, yielded 2. To enhance crystalline property of the polymers, linear alkoxy side chain, 4-heptyloxy group, was introduced at the hydrazide group. Compound 3 was synthesized by dehydrative cyclization of compound 2 using SOCl₂in benzene. Compound 3 was reacted with 2,5dimethyl- phenol in the presence of potassium tert-butoxide in DMF solvent to produce 2-{(heptyloxy)phenyl}-5-(4-(2,5-dimethylphenoxy)phenyl)-1,3,4-oxadiazole, 4. Finally, compound 4 was brominated bezylically using N-bromo-succinimide (NBS) and the free-radical generator, benzoyl peroxide and was purified by column chromatography. All of the synthetic steps produced products in 72.5-86% yield, with the exception of the last step that yielded the monomer, 5, only in the yield of 39%. 2-{4-[2,5-bis(bromomethyl)phenoxy]phenyl-5- $\{4-[heptyloxy]phenyl\}-1,3,4-oxadiazole, 5^{26}$ and $\alpha \alpha'$ dibromo-2-methoxy-5-(2-ethylhexyl-oxy)xylene²⁷ were synthesized according to the procedures from the literature. The homopolymerization of 5 and copolymerization with α, α' -dibromo-2-methoxy-5-(2-ethylhexyl-oxy)xylene were performed with an excess of potassium tertbutoxide in THF at room temperature over a period of 1 hr under a nitrogen atmosphere via a modified Gilch route. 4-methoxy-phenol (2 mol%) was also used in the

polymerization as an initiator to control molecular weight and to circumvent the problem of self-condensation observed for 4-*tert*-butylbenzyl chloride. Hsieh et al. have shown that 4-*tert*-butylbenzyl chloride can be used as an anionic initiator to reduce M_n , but exact control of molecular weight was limited due to self-condensation of the benzyl chloride.²⁸

Most of the PPV homopolymers with electronwithdrawing 1,3,4-oxadiazole units in side chain or main chains are limited in their application, because of their poor solubility and gelation during polymerization.^{29,30} Therefore, to improve the processibility for the device fabrication, copolymerization was carried out with various initial monomer concentrations according to the similar method of homopolymerization. The resulting copolymers, OXH-PPV-*co*-MEH-PPV with various monomers feed ratios showed good solubility behavior in common organic solvents, such as chloroform, chlorobenzene, toluene, THF, xylene, etc.

The TGA thermograms, which were measured at a temperature of 5% weight loss for OXH-PPV, MEH-PPV, and OXH-PPV-*co*-MEH-PPV, showed a thermal stability from 294 to 371 °C. The glass transitions for these polymers was not detected up to degradation temperature and melting temperature by differential scanning calorimetry, which means that the polymers have amorphous structures. Table I summarizes the polymerization results and molecular weights of the homopolymers and copolymers. The number average molecular weight (M_n) and polydispersity values of the present polymers were in the range of $3.5 \sim 16.9 \times 10^4$ and $1.32 \sim 3.74$, respectively.

3.2. Optical and Electrochemical Properties

Figure 2 shows the UV-vis spectra of OXH-PPV, OXH-PPV-co-MEH-PPV, and MEH-PPV (6a-6e) in the solution and film state. Polymers, 6a-6e, had a common feature in their spectra, absorption centered around 304-334 nm and 461-498 nm in the solution state and 307-338 nm and 441-506 nm in the film state, respectively. The absorption in the shorter wavelength region is attributed to the oxadiazole pendant,³¹ and those in the longer wavelength region are attributed to the π - π^* transitions of the main chains. In Figure 2, as the MEH-PPV content decreased (that is, as the oxadiazole unit increased), the absorption maximum (λ_{max}) peak of the 1,3,4-oxadiazole units which represented in the shorter wavelength gradually increased. From this result, it could be assumed that composition ratios (m:n) of copolymers have similar values as compared with feed ratios of monomers by comparing the maximum intensity of the absorption band of the 1,3,4oxadiazole. And, the absorption position for the backbone $\pi - \pi^*$ transition was slightly blue-shifted as increasing the content of repeat unit of polymer 6a, OXH-PPV. This could be explained by a steric effect exerted by the bulky

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Fig. 1. Synthetic scheme for OXH-PPV and its co-polymers with MEH-PPV.

pendant groups present in every repeat unit. That is, it is ascribed to a partial destruction of the π -localization along the backbone by the bulky substituents that disrupt the coplanarity of the π -conjugated backbone.¹⁷

The band gap of OXH-PPV, MEH-PPV, and OXH-PPVco-MEH-PPV, taken from the absorption edge spectrum, was slightly different according to the compositions of copolymers about 2.03–2.31.

	Table I.	Molecular weight and thermal	properties	of OXH-PPV, MEH-PPV,	and OXH-PPV-co-MEH-PPV
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Polymer	M_n^a (g/mol)	M_w^a (g/mol)	PDI^{a}	T_g^{b} (°C)	$T_m^{\ b}$ (°C)	T_d^{c} (°C)
OXH-PPV	_	_	_	_*	_*	294
OXH-PPV-co-MEH-PPV (75:25)	3.8×10^4	5.0×10^{4}	1.32	_*	_*	320
OXH-PPV-co-MEH-PPV (50:50)	3.5×10^4	1.3×10^{5}	3.74	_*	_*	368
OXH-PPV-co-MEH-PPV (25:75)	12.6×10^{4}	4.1×10^{5}	3.28	_*	_*	371
MEH-PPV	16.9×10^4	4.6×10^{5}	2.73	_*	_*	309

Notes: ^aMolecular weight and polydispersity index (PDI) were estimated by GPC against polystylene standards; ^bGlass transition temperature and melting temperature were measured by DSC under nitrogen; ^cTemperature of 5% weight loss were measured by TGA; ${}^{*}T_{g}$ and T_{m} were not detected.

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Fig. 2. UV-visible absorption spectra of OXH-PPV, MEH-PPV, and OXH-PPV-*co*-MEH-PPV in (a) the solution and (b) the film.

PV, MEH-PPV, and PPV-*co*-MEH-PPV in (a) the solution and (b) the film.

Figure 3 shows the photoluminescence spectra of OXH-PPV, OXH-PPV-*co*-MEH-PPV, and MEH-PPV. The polymer films and solutions were excited by the light at the absorption λ_{max} of each polymer. OXH-PPV-*co*-MEH-PPV and MEH-PPV shows similar emission maximum peaks at about 615, 606, 608, and 610 nm. However, the emission peak of OXH-PPV was slightly blue shifted about 31 nm in the solution state and 37 nm in the film state, respectively. It could be seen that such blue-shift was not contributed from OXD groups but was from the reduced content of electron-donating oxygen atom attached to the phenylene ring in the main chain. The characteristic values are listed in Table II.

The oxidation potential of the polymers was measured and calibrated by comparison of the half-wave potential of ferrocene/ferrocenium redox couple. The highest occupied molecular orbital (HOMO) of the resulting polymers was 5.36, 4.96, 4.94, 4.91, and 4.88 eV, respectively. The lowest unoccupied molecular orbital (LUMO) levels were obtained from the values of the band gap calculated from UV-Vis spectra and HOMO level. The band gap of OXH-PPV, OXH-PPV-*co*-MEH-PPV, and MEH-PPV were in the range of 2.03–2.31 eV. The electrochemical characteristics of the present polymers are also summarized in Table II.

3.3. Device Characterizations

3.3.1. OLED Devices

To estimate the emission properties of the resulting polymers as an active layer, devices were fabricated with the configuration ITO/PEDOT:PSS (30 nm)/Polymer (70 nm)/Al (150 nm). Figure 4 shows the current density–voltage–luminance (J-V-L) characteristics of the ITO/PEDOT:PSS/Polymer (6a–6e)/Al devices. The turn-on voltage for the light emission varied from approximately 6.9 V for MEH-PPV to 9.8 V for OXH-PPV-*co*-MEH-PPV (75:25). The current densities of the polymers increased exponentially with an increasing forward bias.

The current–luminescence efficiency and currentquantum efficiency curves of ITO/PEDOT:PSS/Polymer (6b–6e)/Al devices are shown in Figure 5. The luminescence intensities of OXH-PPV, MEH-PPV, and OXH-PPV*co*-MEH-PPV are exponentially increased with an increase in voltage. The maximum luminescence of MEH-PPV is 41 cd/m² at 11.8 V. However, the maximum luminescence of copolymers increased with an increase in the feed ratios of OXH-PPV, and the maximum luminescence of OXH-PPV-*co*-MEH-PPV (50:50) and OXH-PPV-*co*-MEH-PPV (25:75) is 175 cd/m² and 87 cd/m², respectively.

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	UV absorbance		PL				
Polymer	$\overline{\lambda_{\mathrm{ma}}}$ (sol)	λ_{\max} (film)	$\overline{\lambda_{\mathrm{mx}}}$ (sol)	$\lambda_{\rm ma}$ (film)	E_{g}^{a} (eV)	$HOMO^{b}$ (eV)	LUMO (eV)
OXH-PPV	304, 461	307, 441	560	573	2.31	5.36	3.05
OXH-co-MEH-PPV (75:25)	304, 467	309, 461	600	615	2.12	4.96	2.84
OXH-co-MEH-PPV (50:50)	304, 483	318, 474	585	606	2.03	4.94	2.91
OXH-co-MEH-PPV (25:75)	305, 496	320, 499	588	608	2.10	4.91	2.81
MEH-PPV	334, 498	338, 506	591	610	2.09	4.88	2.79

Table II	Optical properties an	d anarow lavals of	OVH DDV MEH DDV	and OVH DDV co MEH DDV
Table II.	Oblical properties an	I energy levels of	UAT-PPV. MET-PPV.	and $OAH-PPV-CO-MEH-PPV$.

Notes: "Determined from the edge of the red end (onset) of absorption spectrum; bDetermined from the onset of the oxidation curve of cyclic voltammetry measurement.

The device performance characteristics of the resulting polymers in ITO/PEDOT:PSS/polymer/Al devices are tabulated in Table III.

Figure 5 shows the luminance efficiency OXH-PPV, MEH-PPV, and OXH-PPV-*co*-MEH-PPV as a function of current density. The highest luminance efficiency of copolymers with a relatively low current density is due to the high LUMO energy level as compared to that of conventional PPV derivatives. The barrier heights of OXH-PPV-*co*-MEHPPV (75:25) OXH-PPV-*co*-MEH-PPV (50:50), and OXH-PPV-*co*-MEH-PPV (25:75) were found to be 1.25, 1.39, and 1.49 at the interface of the Al/LUMO state for electron injection. Thus, easily injected electrons were recombined with the holes in the emitting layer to give high luminance efficiency. These results showed that electron injection was enhanced and balance in carrier.



Fig. 4. (a) J-V and (b) V-L characteristics of OXH-co-MEH-PPV (75:25, 50:50, 25:75) and MEH-PPV.

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Fig. 5. (a) Luminance efficiency and (b) quantum efficiency as a function of current density of OXH-*co*-MEH-PPV (75:25, 50:50, 25:75) and MEH-PPV.

 Table III.
 EL device performance characteristics of the resulting polymers in ITO/ PEDOT: PSS/polymer/Al devices.

Polymer	Turn-on (V)	Quantum efficiency (%)	LE_{\max}^{a} , (cd/A)	L_{\max}^{b} , cd/m ² (@V)
OXH-PPV	5.4	_	_	7 (8.4)
OXH-PPV- <i>co</i> - MEH (75:25)	9.8	0.025	0.026	43 (18.2)
OXH-PPV- <i>co</i> - MEH (50:50)	7.9	0.043	0.082	175 (16.2)
OXH-PPV- <i>co</i> - MEH (25:75)	6.9	0.020	0.028	87 (12.2)
MEH-PPV	6.9	0.010	0.013	41 (11.8)

Notes: ^aMaximum luminescence efficiency; ^bMaximum luminescence.

mobility was improved by introducing electron transport moieties (OXD) on the side chain of the polymer backbones.

3.3.2. OFET Devices

To investigate the switching properties of the resulting polymers as an active layer, devices were fabricated in a top-contact/bottom-gate configuration according to the layer sequence. The fundamental output and transfer characteristics of the devices are shown in Figures 6 and 7, respectively. In Figure 6, the output plots (the drain current I_d as a function of the drain voltage V_d) showed typical *p*-channel organic FETs, being initially linear with



Fig. 6. The output characteristics that were obtained; (a) OXH*co*-MEH-PPV (50:50), (b) OXH-PPV-*co*-MEH-PPV (25:75), and (c) MEH-PPV.



Fig. 7. The transfer characteristics that were obtained; (a) OXH-co-MEH-PPV (50:50), (b) OXH-co-MEH-PPV (25:75), and (c) MEH-PPV.

 V_d and then saturating at higher V_d . The transfer characteristics of the devices were depicted as the I_d values at $V_d = -40$ V to -140 V plotted against the various gate voltages V_g (Fig. 7). The basic parameters in OFETs such as field-effect mobility (μ_{FET}), threshold voltage (V_{th}), and on-off ratio ($I_{\text{on}}/I_{\text{off}}$) are obtained by gradual channel approximation listed in Table IV. The homo-polymer OXH-PPV showed no FET characteristics and MEH-PPV had relatively high μ_{FET} of 6.5×10^{-4} cm²/Vs. Copolymers between OXH-PPV and MEH-PPV also exhibited enhanced μ_{FET} from 2.3×10^{-6} to 3.7×10^{-4} cm²/Vs by increasing the MEH-PPV content from 25% to 75%, respectively. It was mainly attributed that higher HOMO level by incorporation of electron-deficient OXD pendent unit hindered from efficient hole carrier injection.

Moreover, molecular ordering and $\pi - \pi$ overlap interaction between the adjacent molecules were also presumably deteriorated due to big-sized OXD pendent group directly in polymer backbone.

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Table IV. Fundamental OFET properties that were obtained in this experiment; mobility, threshold voltage, and on/off ratio, where W = 1.5 mm and $L = 50 \ \mu\text{m}$.

Polymer	Mobility (cm ² /Vs)	Threshold voltage V_{Th} (V)	On/off ratio $(I_{\rm on}/I_{\rm off})$
OXH-PPV	_	_	_
OXH-PPV-co-MEH- PPV (75:25)	2.3×10^{-6}	-46	$\sim 10^2$
OXH-PPV- <i>co</i> -MEH- PPV (50:50)	$7.0 imes 10^{-5}$	-50	$\sim 10^4$
OXH-PPV- <i>co</i> -MEH- PPV (25:75)	3.7×10^{-4}	-38	$\sim 10^5$
MEH-PPV	$6.5 imes 10^{-4}$	-41	$\sim 10^4$

Although the OXH-PPV, OXH-PPV-co-MEH-PPV, and MEH-PPV materials showed no ambipolar charge transport behavior, the electron-rich (PPV moiety) and electrondeficient (OXD) moieties in the polymer backbone enabled to be potentially ambipolar charge transport. In fact, most of π -conjugated organic semiconductors have intrinsically ambipolar or bipolar charge transport capability, but the *n*-channel properties frequently hided from extrinsic effects, such as dielectrics, passivation, and/or source/drain contact. It is noted that no n-channel properties of those materials observed because the OFET devices in present study had bottom gate (SiO₂ dielectric and doped Si gate) and top-contact (Au) structure. The SiO₂ is commonly known as strong electron traps due to its hydroxyl (-O-H) group on SiO2 surface, and the high work function (~ -5.1 eV) Au electrode also lead to unbalanced electron and hole injection efficiency. We believe that other device structure, such as top-gate (hydroxyl-free polymer dielectrics such as poly(methyl methacrylate))/bottom-contact (Au) or bottom-gate (BCBcoated or SAM-treated SiO₂)/dissimilar top electrodes (Au and Ca), enable to show the ambipolar properties. The MEH-PPV OFET already reported ambipolar charge transport¹⁷ and applied to OLEFETs.³³ High performance ambipolar OFETs and high efficiency light-emitting transistors are currently under study in our group.

4. CONCLUSION

New polymers incorporating an oxadiazole moiety with controlled molecular weight as a fully conjugated side chain to poly(*p*-phenylene vinylene) PPV backbone were successfully synthesized via a modified Gilch route in the presence of an initiator. Polymer films could be easily fabricated by spin-coating because polymers were dissolved in common solvents. To investigate the possibility of application for OLEFET using these polymers as active materials, device performance of OLEDs and OFETs were studied. Electrochemical properties and device performance could be controlled by adjusting the feed ratio of the OXD content through copolymerization. Single-layer EL devices with a stable metal (Al) as cathode

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were successfully fabricated. The improved device performance of OXH-PPV and OXH-PPV-*co*-MEH-PPV over MEH-PPV may be due to better electron injection and charge balance between holes and electrons and efficient intramolecular energy transfer from OXD units to the PPV backbones as well. The maximum luminescence and the luminescene efficiency of the polymers were up to 175 cd/m² and 0.082 cd/A at 16.2 V, respectively. And, to investigate the switching properties of the resulting polymers as an active layer, devices were fabricated in a top-contact/bottom-gate configuration. The resulting FETs exhibited typical *p*-channel characteristics. The mobilities in the saturation regime were in the range of about $6.5 \times 10^{-4} \sim 7.0 \times 10^{-5}$ cm²/Vs, and on-off ratios were about $10^4 \sim 10^5$.

From these results, the present copolymers showed OLED and OFET characteristics that is required for efficient OLEFET devices. Therefore, copolymer systems of these materials could be new candidates for active materials in OLEFETs.

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