# Poly(*p*-phenylenevinylene)s Derivatives Containing a New Electron-Withdrawing $CF_3F_4$Phenyl Group for LEDs

**Youngeup Jin, Jeung Hee Kang,† Suhee Song, Sung Heum Park,‡ Jihyun Moon,**
**Han Young Woo,§ Kwanghee Lee,‡ and Hongsuk Suh***

*Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Korea*
**E-mail: hssuh@pusan.ac.kr*
*†Samsung Electronics Co., Maetan-dong, Yeongtong-gu, Suwon, Gyeonggi 443-742, Korea*
*‡Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea*
*§Department of Nanomaterials Engineering, Pusan National University, Miryang 627-706, Korea*
*Received October 17, 2007*

New PPV derivatives which contain electron-withdrawing $CF_3F_4$phenyl group, poly[2-(2-ethylhexyloxy)-5-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-1,4-phenylenevinylene] ($CF_3F_4$P-PPV), and poly[2-(4-(2-etylhexyloxy)-phenyl)-5-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-1,4-phenylenevinylene] (P-$CF_3F_4$P-PPV), have been synthesized by GILCH polymerization. As the result of the introduction of the electron-withdrawing $CF_3F_4$phenyl group to the phenyl backbone, the LUMO and HOMO energy levels of $CF_3F_4$P-PPV (3.14, 5.50 eV) and P-$CF_3F_4$P-PPV (3.07, 5.60 eV) were reduced. The PL emission spectra in solid thin film are more red-shifted over 50 nm and increased fwhm (full width at half maximum) than solution conditions by raising aggregation among polymer backbone due to electron withdrawing effect of 2,3,5,6-tetrafluoro-4-trifluoromethylphenyl group. The EL emission maxima of $CF_3F_4$P-PPV and P-$CF_3F_4$P-PPV appear at around 530-543 nm. The current density-voltage-luminescence (J-V-L) characteristics of ITO/PEDOT/polymer/Al devices of $CF_3F_4$P-PPV and P-$CF_3F_4$P-PPV show that turn-on voltages are around 12.5 and 7.0 V, and the maximum brightness are about 82 and 598 cd/m$^2$, respectively. The maximum EL efficiency of P-$CF_3F_4$P-PPV (0.51 cd/A) was higher than that of $CF_3F_4$P-PPV (0.025 cd/A).

**Key Words :** Electroluminescence, PPV, Electron-withdrawing group, Polymer light emitting diodes (PLEDs)

## Introduction

For the use in full color plat panel displays, one of the most promising candidate is organic light-emitting diode (OLED) with several advantages over conventional devices such as a low driving voltage, wide viewing angle, thin film structure, and a simpler manufacturing process.[1] Caused by the prospective applications as large-area light emitting diodes (LEDs),[2-6] numerous reports about polymer light-emitting diodes (PLEDs) have been published since the discovery of electroluminescence (EL) from conjugated polymers.[7-11] Most of the research in the field of polymer-based electroluminescent devices has been focused on main-chain conducting polymers such as poly(plenylenevinylene) (PPV),[12] poly(p-phenylene) (PPP),[13] poly(thiophene),[14] poly(fluorene),[15] their copolymers and soluble derivatives.

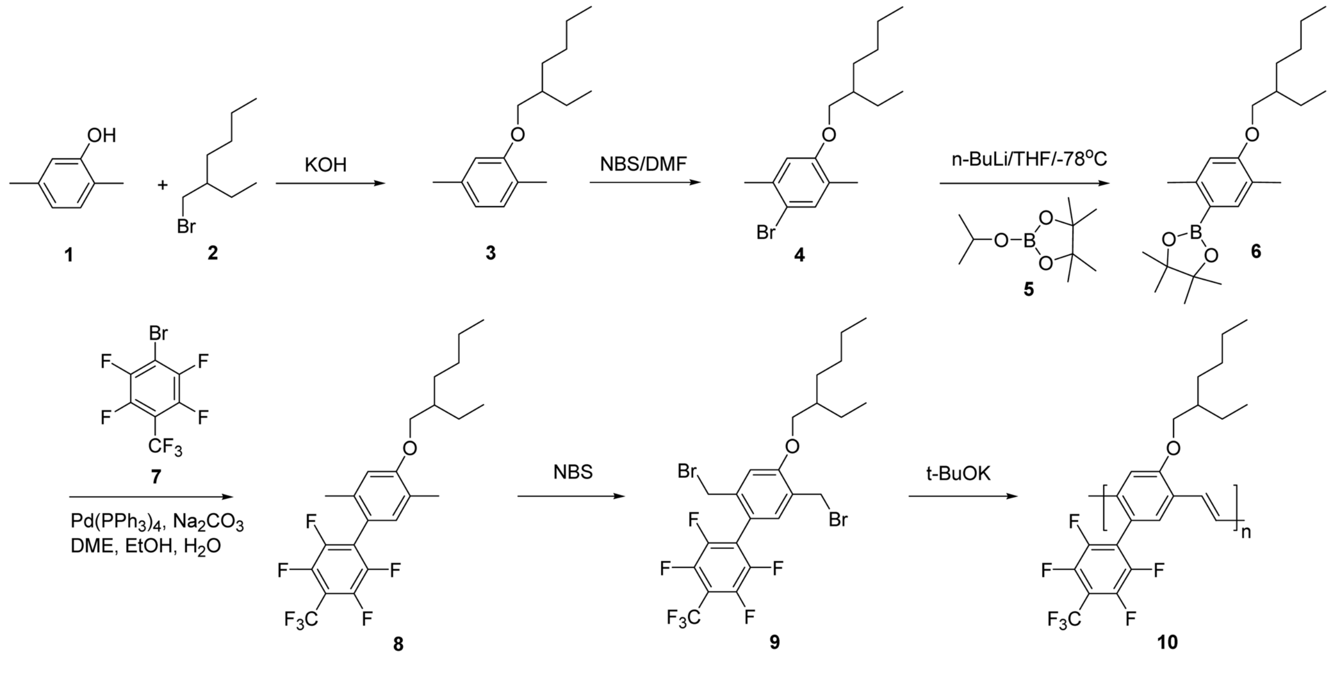
In conjugated polymers, EL is known to be generated by the injection of electrons from one electrode and holes from the other, recombination, and radiative decay of the excited state. It has been known that recombination of electrons and holes injected from cathode and anode produce emission in the luminescent polymer layer of the LEDs. Balanced charge injection from both electrodes and comparable mobility of both charge carrier types are important for high device efficiencies.[16-18] To be used in the single layer devices with high work function metal as the cathode, PPV has the disadvantage that it is a poor electron acceptor due to its high LUMO energy. The high LUMO energy level usually causes the imbalance of charge injections and poor device efficiency. Balancing the rates of injection of electrons and holes from opposite electrodes into the light-emitting polymer is required to achieve the high electroluminescence efficiency. Using additional organic charge-transporting layers,[19,20] and adjusting the energy band of the polymer by introduction of electron-withdrawing groups attached to the polymer backbone[21,22] were reported to overcome the imbalance of charge carrier injection or mobility. It was reported that the HOMO and LUMO energy levels can be lowered by the introduction of electron-withdrawing groups onto the arylene rings or the vinylene groups of the polymer.[23] To improve the electron injection and the potential efficiency of the polymer LEDs, numerous derivatives of PPV with halide,[24-28] cyano,[29] trifluoromethyl,[30] and methylsulfonyl-phenyl[31] on the arylene rings, or on vinylene,[32-35] have been reported.

The present investigation deals with the synthesis, characterization, photophysics, and electroluminescence (EL) of a new copolymers which contain electron-withdrawing $CF_3F_4$-phenyl group, poly[2-(2-ethylhexyloxy)-5-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-1,4-phenylenevinylene] ($CF_3F_4$P-PPV), and poly[2-(4-(2-etylhexyloxy)-phenyl)-5-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-1,4-phenylenevinylene] (P-$CF_3F_4$P-PPV). The new polymers were synthesized by Gilch polymerization.[36] $CF_3F_4$phenyl group is the one of the strongest electron-withdrawing group which can be introduced in PPV. We can expect that the strong electron-withdrawing $CF_3F_4$phenyl group can make lower HOMO and LUMO energy levels, and get balanced charge injection and mobility on the physical and electrochemical properties of $CF_3F_4$P-PPV and P-$CF_3F_4$P-PPV.

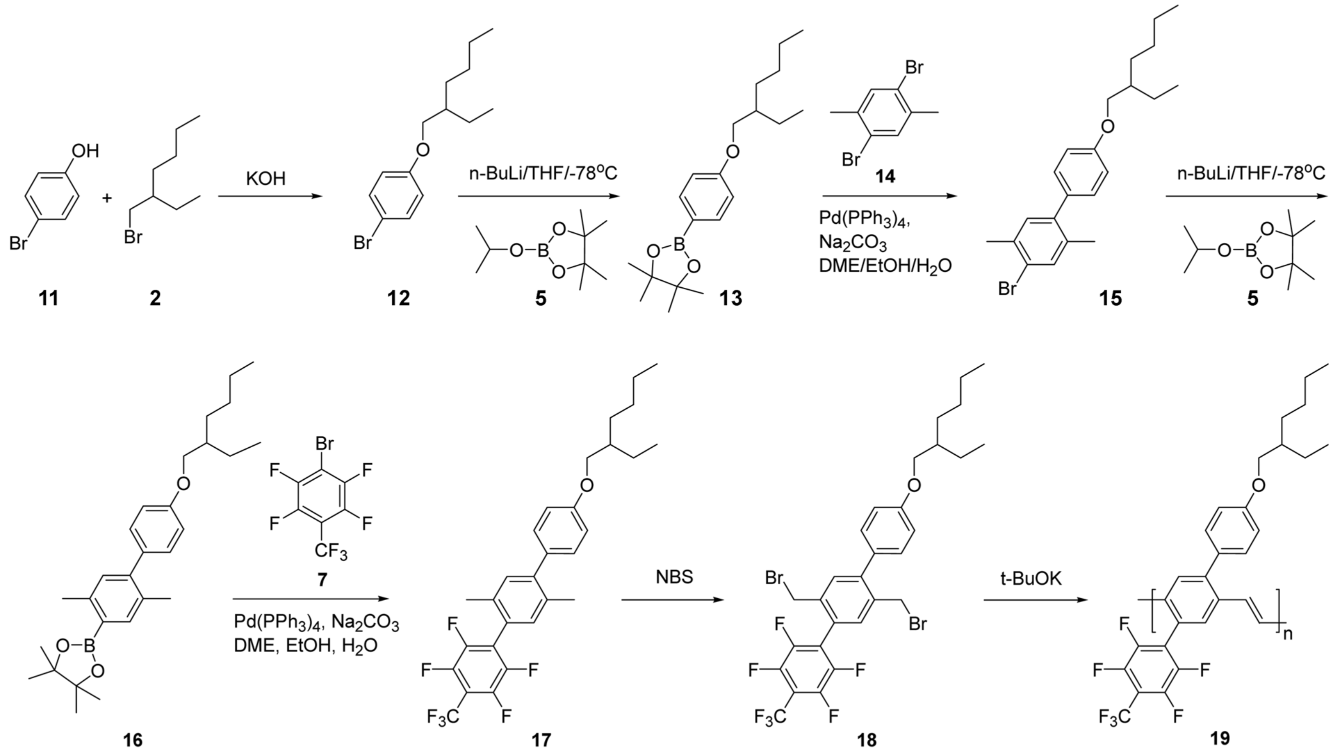
## Experimental Section

**General.** Used all reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. $^1$H and $^{13}$C NMR spectra were recorded with a Varian Gemini-200 (200 MHz) spectrometer and chemical shifts were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminium plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. The PL and EL spectra of the device were measured using an Oriel InstaSpec IV CCD detection systems. For PL spectrum measurements, xenon lamp was used as the excitation source, and incident beam took the maximum absorption peak of the polymers. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s. The CV was performed in a solution of tetrabutylammonium tetrafluoroborate ($Bu_4NBF_4$) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode (~0.05 cm$^2$) coated with a thin polymer film was used as the working electrode. A Pt wire and a Ag/$AgNO_3$ electrode were used as the counter electrode and reference electrode, respectively. All measurements were calibrated against an internal standard, ferrocene ($F_c$), which has the IP value (–4.8 eV) for the $F_c/F_c^+$ redox system. For the EL experiment of PLEDs with configuration of ITO/PEDOT/polymers/Ca/Al, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. Isopropyl solution of the PEDOT/PSS was spin-coated on the surface-treated ITO substrate. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting ODCB (*o*-dichlorobenzene) solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in vacuum, and calcium and aluminum electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below $10^{-7}$ Torr, yielding active areas of 4 mm$^2$. For the determination of device characteristics, current-voltage (I-V) characteristics were measured using a Keithley 236 source measure unit. All processing steps and measurements mentioned above were carried out under air and at room temperature.

**Synthesis of 2-[(2-Ethylhexyl)oxy]-1,4-dimethylbenzene (3).** To a stirred solution of 10 g (81.85 mmol) of 2-hydroxy-*p*-xylene (**1**), 5.95 g (90.05 mmol) of potassium hydroxide, and 1.25 g (8.2 mmol) of sodium iodide was added the solution of 16.7 mL (90.05 mmol) of 2-ethylhexyl bromide (**2**) in 200 mL of ethyl alcohol. After being refluxed for 3 days, the reaction mixture was cooled and filtered. The mixture was concentrated *in vacuo*, diluted with 300 mL of



**Scheme 1**. Synthetic routes for $CF_3F_4$P-PPV.



**Scheme 2**. Synthetic routes for P-$CF_3F_4$P-PPV.

ethyl acetate, and washed with 2 × 30 mL of water and with 30 mL of saturated sodium chloride solution. The organic layer was dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The resulting product was purified by silica gel chromatography ($R_f$ 0.5, hexane 100%) to give 17.65 g (92%) of desired product **3**. $^1$H-NMR (200 MHz, $CDCl_3$): $\delta$(ppm) 0.89-0.99 (m, 6H), 1.29-1.56 (m, 8H), 1.74 (m, 1H), 2.19 (s, 3H), 2.33 (s, 3H), 3.87 (d, 2H, $J$ = 26 Hz), 6.67 (s, 1H), 6.69 (d, 2H, $J$ = 31 Hz), 7.04 (d, 2H, $J$ = 38 Hz). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta$ (ppm) 11.21, 14.04, 15.75, 21.38, 23.04, 24.10, 29.11, 30.72, 39.59, 70.02, 111.73, 120.38, 123.66, 130.17, 136.40, 157.27.

**Synthesis of 1-Bromo-4-[(2-ethylhexyl)oxy]-2,5-dimethylbenzene (4).** To a stirred solution of 17.65 g (75.3 mmol) of 2-[(2-ethylhexyl)oxy]-1,4-dimethylbenzene (**3**) in 200 mL of DMF at room temperature under argon was added 16.1 g (90.3 mmol) of NBS. The reaction mixture was stirred for 2 h at room temperature, and concentrated under reduced pressure. The reaction mixture was diluted with 300 mL of ethyl acetate, and washed with 5 × 30 mL of water. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography ($R_f$ 0.6, hexane 100%) to give 16.2 g (68.65%) of desired product **4**. $^1$H-NMR (200 MHz, $CDCl_3$): $\delta$(ppm) 0.78-0.97 (m, 6H), 1.27-1.57 (m, 8H), 1.73 (m, 1H), 2.16 (s, 3H), 2.35 (s, 3H), 3.81 (d, 2H, $J$ = 26 Hz), 6.68 (s, 1H), 7.26 (s, 1H). $^{13}$C-NMR (50 MHz, $CDCl_3$): $\delta$ (ppm) 11.19, 14.05, 15.47, 22.85, 23.04, 24.07, 29.10, 30.68, 39.52, 70.42, 113.28, 114.25, 126.33, 133.52, 135.52, 156.57.

**Synthesis of 2-Isopropoxy-4,4,5,5-tetramethyl-[1.3.2]-dioxaborolane (6).** To a stirred solution of 3 g (9.57 mmol) of 1-bromo-4-(2-ethylhexyloxy)-2,5-dimethylbenzene (**4**) in dry THF (30 mL) under argon atmosphere at –78 °C was added 7.16 mL (11.49 mmol) of *n*-BuLi (1.6 M *n*-hexane solution). After the addition of *n*-BuLi, the mixture was stirred at –78 °C for 30 min. To the reaction mixture 1.15 mL (10.05 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added drop-wise at –78 °C. The solution was allowed to warm to room temperature and stirred for an additional 2 h. The reaction mixture was quenched by water, and extracted with ether. The solvent was removed by evaporation under reduced pressure. The yellow oil was purified by column chromatography ($R_f$ 0.4, EtOAc:hexane = 1:10) to provide the desired final borolane product **6** as yellow oil (1.2 g, 35%). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta$(ppm) 0.91-0.98 (m, 6H), 1.25-1.57 (m, 8H), 1.80 (m, 1H), 2.27 (s, 3H), 2.81 (s, 3H), 3.95 (d, 2H, $J$ = 27 Hz), 6.73 (s, 1H), 7.98 (s, 1H).

**Synthesis of 4'-(2-Ethyl-hexyloxy)-2,3,5,6-tetrafluoro-2',5'-dimethyl-4-trifluoromethylbiphenyl (8).** To a stirred solution of 1.2 g (4.31 mmol) of borolane compound **6** in 15 mL of DME (1,2-dimethoxyethane), 15 mL of ethyl alcohol, and 15 mL of aqueous $Na_2CO_3$ (2 M) was added 1.24 g (4.31 mmol) of 1-bromo-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene (**7**). After the solution was purged with nitrogen for 20 min, 0.24 g (0.21 mmol) of tetrakis(triphenylphosphine) palladium (0) ($Pd[P(Ph)_3]_4$) was added. The reaction mixture was refluxed with vigorous stirring under nitrogen for 24 h. The reaction mixture was diluted with ethyl acetate and water. The organic phase was separated and washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography ($R_f$ 0.40, EtOAc:Hex = 1:10) to give 1.2 g (62%) of product **8** as white solid. $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ (ppm) 0.94-1.02 (m, 6H), 1.35-1.59 (m, 8H), 1.78 (m, 1H), 2.19 (s, 3H), 2.24 (s, 3H), 3.93 (d, 2H, $J$ = 28 Hz), 6.81 (s, 1H), 6.94 (s, 1H).

**Synthesis of 2',5'-Bis-bromomethyl-4'-(2-ethyl-hexyloxy)2,3,5,6-tetrafloro-4-trifluoromethylbiphenyl (9).** To a stirred solution of 1 g (2.24 mmol) of compound **8**, and 0.88 g (4.93 mmol) of NBS in 25 mL of CCl$_4$ at room temperature was emitted the light source for 1 h. The reaction mixture was filtered in order to remove succinimide. The reaction mixture was concentrated *in vacuo*, and purified by column chromatography ($R_f$ 0.2, hexane 100%) to provide the desired final brominated product **6** as white solid (0.4 g, 29%). $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ (ppm) 0.92-1.01 (m, 6H), 1.25-1.59 (m, 8H), 1.82 (m, 1H), 4.00 (d, 2H, $J$ = 27 Hz), 4.29 (s, 2H), 4.51 (s, 2H), 7.07 (s, 1H), 7.19 (s, 1H).

**Synthesis of CF$_3$F$_4$P-PPV (10).** To a stirred solution of 300 mg (0.49 mmol) of monomer **9** in dry THF (50 mL) was added 3.0 mL (3.0 mmol) of potassium *tert*-butoxide (1.0 M THF solution) by a syringe pump over 1 h. During the addition, the reaction mixture had color change from colorless *via* yellow to orange, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred additionally for 12 h at room temperature. The reaction mixture was poured into 500 mL of methanol with stirring. The precipitated polymer was filtered off, and the resulting polymer was dissolved again in THF. The dissolving polymer was slowly poured into 500 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with water, and dried under reduced pressure at room temperature. A 100 mg sample of polymer **10** was obtained as orange fiber. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ (ppm) 0.89-0.97 (br, 6H), 1.25-1.46 (br, 8H), 1.78 (br, 1H), 4.00 (br, 2H), 6.75-7.45 (br, 4H). FTIR (KBr): 3009, 2677, 2013, 1844, 1612, 1512, 1443, 1365, 1319, 1250.

**Synthesis of 1-Bromo-4-(2-ethylhexyloxy)benzene (12).** To a stirred solution of 10 g (57.80 mmol) of 4-bromophenol (**11**), 4.57 g (63.36 mmol) of potassium hydroxide, and 0.87 g (5.8 mmol) of sodium iodide was added the solution of 11.24 mL (60.69 mmol) of 2-ethylhexyl bromide (**2**) in 150 mL of ethyl alcohol. After being refluxed for 3 days, the reaction mixture was cooled and filtered. The mixture was concentrated *in vacuo*, diluted with 300 mL of ethyl acetate, and washed with 2 × 30 mL of water and with 30 mL of saturated sodium chloride solution. The organic layer was dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The resulting product was purified by silica gel chromatography ($R_f$ 0.6, hexane 100%) to give 12.5 g (76%) of desired product **12**. $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ (ppm) 0.88-1.00 (m, 6H), 1.21-1.56 (m, 8H), 1.68 (m, 1H), 3.80 (d, 2H, $J$ = 28 Hz), 6.77 (d, 2H, $J$ = 44 Hz), 7.36 (d, 2H, $J$ = 46 Hz).

**Synthesis of 2-[4-(2-Ethylhexyloxy)phenyl]-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane (13).** To a stirred solution of 9 g (41.44 mmol) of 1-bromo-4-(2-ethylhexyloxy)benzene (**12**) in dry THF (50 mL) under argon atmosphere at –78 °C was added 28.5 mL (45.6 mmol) of *n*-BuLi (1.6 M *n*-hexane solution). After the addition of *n*-BuLi, the mixture was stirred at –78 °C for 30 min. To the reaction mixture 10.3 mL (49.72 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added drop-wise at –78 °C. The solution was allowed to warm to room temperature and stirred for an additional 2 h. The reaction mixture was quenched by water, and extracted with ether. The solvent was removed by evaporation under reduced pressure. The yellow oil was purified by column chromatography ($R_f$ 0.33, EtOAc:hexane = 1:20) to provide the desired final borolane product **13** as yellow oil (12.5 g, 91%). $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ (ppm) 0.88-0.95 (m, 6H), 1.32 (s, 12H), 1.23-1.45 (m, 8H), 1.68 (m, 1H), 3.86 (d, 2H, $J$ = 39 Hz), 6.88 (d, 2H, $J$ = 42 Hz), 7.73 (d, 2H, $J$ = 44 Hz).

**Synthesis of 4-Bromo-4'(2-ethylhexyloxy)-2,5-dimethylbiphenyl (15).** To a stirred solution of 15.89 g (60.2 mmol) of 1,4-dibromo-2,5-dimethylbenzene (**14**) in 100 mL of DME (1,2-dimethoxyethane), 50 mL of ethyl alcohol, and 50 mL of aqueous Na$_2$CO$_3$ (2 M) was added 10 g (30.1 mmol) of 2-[4-(2-ethylhexyloxy)phenyl]-4,4,5,5-tetramethyl-[1,3,2] dioxaborolane (**13**). After the solution was purged with nitrogen for 20 min, 3.48 g (3.01 mmol) of tetrakis-(triphenylphosphine) palladium (0) (Pd[P(Ph)$_3$]$_4$) was added. The reaction mixture was refluxed with vigorous stirring under nitrogen for 24 h. The reaction mixture was diluted with ethyl acetate and water. The organic phase was separated and washed with brine and dried over MgSO$_4$. The crude product was purified by column chromatography ($R_f$ 0.40, EtOAc:Hex = 1:50) to give 3 g (26%) of product **15** as white solid. $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ (ppm) 0.95-1.01 (m, 6H), 1.37-1.57 (m, 8H), 1.77 (m, 1H), 2.23 (s, 3H), 2.40 (s, 3H), 3.90 (d, 2H, $J$ = 30 Hz), 6.96 (d, 2H, $J$ = 42 Hz), 7.01 (s, 1H), 7.21 (d, 2H, $J$ = 42 Hz), 7.44 (s, 1H).

**Synthesis of 2-[4'-(2-Ethylhexyloxy)-2,5-dimethylbiphenyl-4-yl-4,4,5,5-tetramethyl-[1,3,2] Dioxaborolane (16).** To a stirred solution of 3 g (7.70 mmol) of 4-bromo-4'(2-ethylhexyloxy)-2,5-dimethylbiphenyl (**15**) in dry THF (50 mL) under argon atmosphere at –78 °C was added 5.3 mL (8.48 mmol) of *n*-BuLi (1.6 M *n*-hexane solution). After the addition of *n*-BuLi, the mixture was stirred at –78 °C for 30 min. To the reaction mixture 1.86 mL (9.2 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added drop-wise at –78 °C. The solution was allowed to warm to room temperature and stirred for an additional 2 h. The reaction mixture was quenched by water, and extracted with ether. The solvent was removed by evaporation under reduced pressure. The yellow oil was purified by column chromatography ($R_f$ 0.5, EtOAc:hexane = 1:20) to provide the desired final borolane product **16** as yellow oil (1.6 g, 48%). $^1$H-NMR (200 MHz, CDCl$_3$): $\delta$ (ppm) 0.88-0.98 (m, 6H), 1.35 (S, 12H), 1.41-1.56 (m, 8H), 1.77 (m, 1H), 2.25 (s, 3H), 2.52 (s, 3H), 3.87 (d, 2H, $J$ = 27 Hz), 6.93 (d, 2H, $J$ = 44 Hz), 7.04 (s, 1H), 7.23 (d, 2H, $J$ = 44 Hz), 7.66 (s, 1H).

**Synthesis of 4-(2-Ethylhexyloxy)-2",3",5",6"-tetrafluoro-2',5'-dimetyl-4"-trifluoromethyl-[1,1',4',1"] terphenyl (17).** To a stirred solution of 2.74 g (18.4 mmol) of borolane compound **16** in 60 mL of DME (1,2-dimethoxyethane), 30 mL of ethyl alcohol, and 30 mL of aqueous $Na_2CO_3$ (2 M) was added 4 g (9.17 mmol) of 1-bromo-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene (**7**). After the solution was purged with nitrogen for 20 min, 0.5 g (0.92 mmol) of tetrakis(triphenylphosphine) palladium (0) (Pd-$[P(Ph)_3]_4$) was added. The reaction mixture was refluxed with vigorous stirring under nitrogen for 24 h. The reaction mixture was diluted with ethyl acetate and water. The organic phase was separated and washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography ($R_f$ 0.35, EtOAc:Hex = 1:50) to give 1.5 g (31%) of product **17** as white solid. $^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ (ppm) 0.82-0.92 (m, 6H), 1.11-1.56 (m, 8H), 1.77 (m, 1H), 2.18 (s, 3H), 2.28 (s, 3H), 3.89 (d, 2H, $J$ = 28 Hz), 6.96 (d, 2H, $J$ = 42 Hz), 7.08 (s, 1H), 7.23 (d, 2H, $J$ = 42 Hz), 7.30 (s, 1H).

**Synthesis of 2',5'-Bis-bromomethyl-4-(2-ethylhexyloxy)-2",3",5",6"-tetrafluoro-4"-trifluoromethyl-[1,1',4',1"]terphenyl (18).** To a stirred solution of 1.5 g (2.85 mmol) of compound **17**, and 1.18 g (6.26 mmol) of NBS in 50 mL of $CCl_4$ at room temperature was emitted the light source for 1 h. The reaction mixture was filtered in order to remove succinimide. The reaction mixture was concentrated *in vacuo*, and purified by column chromatography ($R_f$ 0.4, EtOAc:Hex = 1:20) to provide the desired final brominated product **18** as white solid (0.8 g, 41%). $^1$H-NMR (200 MHz, $CDCl_3$): $\delta$ (ppm) 0.87-0.99 (m, 6H), 1.26-1.55 (m, 8H), 1.76 (m, 1H), 3.90 (d, 2H, $J$ = 28 Hz), 4.33 (s, 2H), 4.46 (s, 2H), 6.97 (d, 2H, $J$ = 42 Hz), 7.03 (s, 1H), 7.25 (d, 2H, $J$ = 42 Hz), 7.39 (s, 1H).

**Synthesis of P-$CF_3F_4$P-PPV (19).** To a stirred solution of 300 mg (0.44 mmol) of monomer **18** in dry THF (50 mL) was added 3.0 mL (3.0 mmol) of potassium *tert*-butoxide (1.0 M THF solution) by a syringe pump over 1 h. During the addition, the reaction mixture had color change from colorless *via* yellow to orange, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred additionally for 12 h at room temperature. The reaction mixture was poured into 500 mL of methanol with stirring. The precipitated polymer was filtered off, and the resulting polymer was dissolved again in THF. The dissolving polymer was slowly poured into 500 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with water, and dried under reduced pressure at room temperature. A 120 mg sample of polymer **19** was obtained as orange fiber. $^1$H-NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 0.91 (br, 6H), 1.32 (br, 8H), 1.73 (br, 1H), 3.86 (br, 2H), 6.94-7.25 (br, 8H). FTIR (KBr): 3009, 2677, 1967, 1597, 1504, 1442, 1319, 1257, 1195.

## Results and Discussion

**Synthesis and Characterization.** The general synthetic routes toward the monomers and polymers are outlined in Scheme 1 and 2. In the first step, 2-hydroxy-*p*-xylene (**1**) was coupled with 2-ethylhexyl bromide (**2**) using potassium hydroxide in ethyl alcohol. 2-[(2-Ethylhexyl)oxy]-1,4-dimethylbenzene (**3**) was brominated at the *para*-position with NBS in DMF. The resulting bromide compound **4** was treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) and n-butyl lithium in THF to generate borolane compound **6**, which was coupled with 1-bromo-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene (**7**) using tetrakis(triphenylphosphine) palladium (0) ($Pd[P(Ph)_3]_4$) catalyst and sodium carbonate in DME and water by Suzuki coupling. The compound **8** was brominated at the benzyl positions with NBS and light source (300W) in $CCl_4$ to generate monomer **9**. The polymer, $CF_3F_4$P-PPV (**10**), was prepared by the Gilch reaction, with the monomer **9**, and an excess amount of potassium *tert*-butoxide in THF at 0 °C for 24 h under argon atmosphere. In order to synthesize P-$CF_3F_4$P-PPV (**19**), 4-bromophenol (**11**) was coupled with 2-ethylhexyl bromide (**2**) using potassium hydroxide in ethyl alcohol. 1-Bromo-4-(2-ethylhexyloxy)benzene (**12**) was treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) and n-butyl lithium in THF to generate borolane compound **13**, which was coupled with 1,4-dibromo-2,5-dimethylbenzene (**14**) using tetrakis(triphenylphosphine) palladium (0) ($Pd[P(Ph)_3]_4$) catalyst and sodium carbonate in DME and water by Suzuki coupling. The compound **15** was treated with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**) and n-butyl lithium in THF to generate borolane compound **16**, which was coupled with 1-bromo-2,3,5,6-tetrafluoro-4-trifluoromethylbenzene (**7**) using tetrakis(triphenylphosphine) palladium (0) ($Pd[P(Ph)_3]_4$) catalyst and sodium carbonate in DME and water by Suzuki coupling. The compound **17** was brominated at the benzyl positions with NBS and light source (300W) in $CCl_4$ to generate monomer **18**. The polymer, P-$CF_3F_4$P-PPV (**19**), was prepared by the Gilch reaction, with the monomer **18**, and an excess amount of potassium *tert*-butoxide in THF at 0 °C for 24 h under argon atmosphere.

The resulting $CF_3F_4$P-PPV and P-$CF_3F_4$P-PPV, brittle yellow polymers were soluble in organic solvents such as chloroform, chlorobenzene, THF, MC and *o*-dichlorobenzene (ODCB). The emissive polymer films were obtained by spin-casting an ODCB solution of the polymers. The results of polymerization of $CF_3F_4$P-PPV and P-$CF_3F_4$P-PPV are summarized in Table 1. The number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$), and the polydispersities (PDI) of $CF_3F_4$P-PPV were 31000, 157000, and 5.1, and in case of P-$CF_3F_4$P-PPV, they were 52000, 106000, and 2.1, as determined by GPC using THF as the

**Table 1**. Polymerization results and thermal properties of the polymers

| polymer | $M_n^a$ ($\times 10^3$) | $M_w^a$ ($\times 10^3$) | PDI$^a$ | $T_d^b$ (°C) |
|---|---|---|---|---|
| $CF_3F_4$P-PPV | 31 | 157 | 5.1 | 239 |
| P-$CF_3F_4$P-PPV | 52 | 106 | 2.1 | 247 |

[a] $M_n$ , $M_w$, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards. [b] $T_d$ were measured at a temperature of 5 % weight loss for the polymers by TGA.

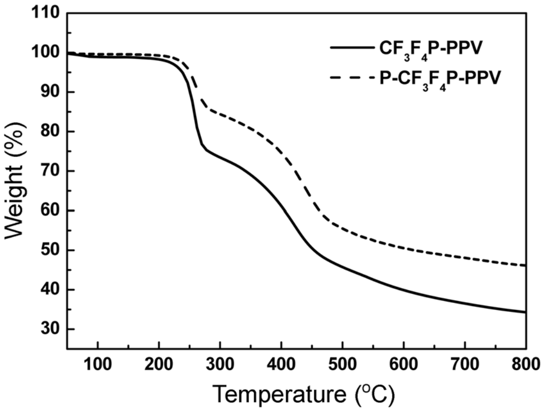


**Figure 1**. TGA curves for $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV.

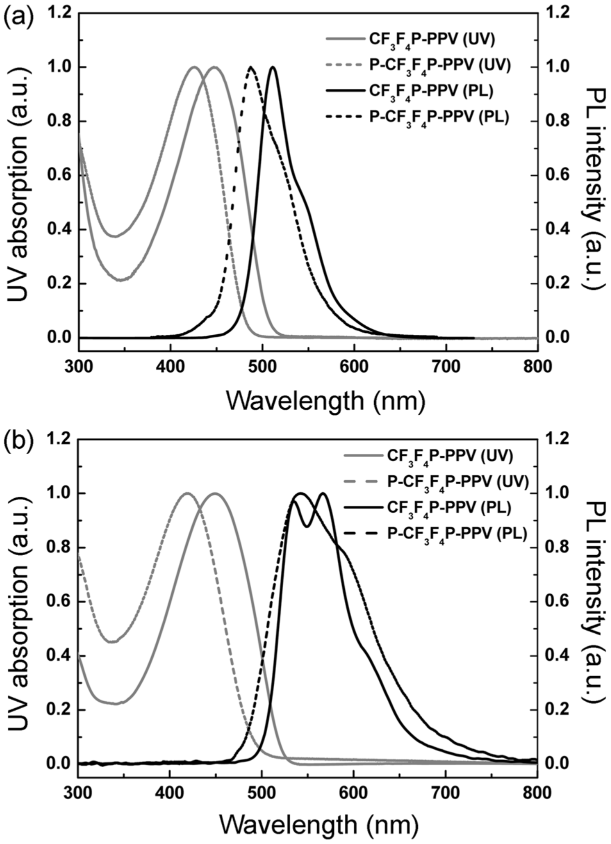


**Figure 2**. UV-visible absorption and PL spectra of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV in solution (a) and in thin film state (b).

eluant and polystyrene as the standard. The thermal properties of the polymers were determined by thermal gravimetric analysis (TGA) under a nitrogen atmosphere at a heating rate of 10 °C/min. $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV lose less than 5% of their weights on heating to 239 °C and 247 °C, respectively. These $T_d$ data are lower than general PPV derivatives. We can estimate that the possession of both electron-donating alkoxy group and electron-withdrawing $CF_3F_4$phenyl group in polymer backbone can reduce the thermal stability. However, it is sufficient that the thermal stability of the resulting polymers prevents the deformation of the polymer morphology and degradation of the polymer light-emitting device by applied electric field of the LED.

**Table 2**. Optical properties of the polymers

| polymer | solution (nm) | | | film $\lambda_{max}$ (nm) | | |
|---|---|---|---|---|---|---|
| | Abs $\lambda_{max}$ | PL $\lambda_{max}$ | fwhm[a] | Abs $\lambda_{max}$ | PL $\lambda_{max}$ | fwhm[a] |
| $CF_3F_4P$-PPV | 447 | 511 | 53 | 449 | 535, 566 | 82 |
| P-$CF_3F_4P$-PPV | 426 | 487 | 65 | 418 | 542 | 115 |

[a] Full width at half-maximum of PL Spectra in the solution and film

**Optical and Photoluminescence Properties.** Figure 2 shows the absorption and photoluminescence (PL) (exciting wavelength, 420 nm) spectra for $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV in solution and thin film which are summarized in Table 2. The solution was prepared using THF as solvent and the thin film was prepared by spin-coating on quartz plates from the polymer solutions in ODCB. The maximum absorption peaks of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV appear at around 447 and 426 nm in THF solution. The spectrum of P-$CF_3F_4P$-PPV was more blue-shifted than $CF_3F_4P$-PPV. The maximum absorption peaks of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV in solid thin film were almost similar with solution for around 449 and 418 nm. The absorption onset wavelengths of all polymers were around 525 and 490 nm, which correspond to band gaps of 2.36 and 2.53 eV. The conjugation length of $CF_3F_4P$-PPV is longer than P-$CF_3F_4P$-PPV, since the electron donating effect of directly attached alkoxy group in backbone of $CF_3F_4P$-PPV is higher than phenyl alkoxy group of P-$CF_3F_4P$-PPV.

The PL emission spectra of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV in THF solution show a maximum peak at 511 and 487 nm. In case of solid thin film, they are more red-shifted over 50 nm than solution conditions, and the full width at half maximum (fwhm) was increased, which can be contributed to the increased $\pi$-$\pi^*$ interaction. The PL spectra of $CF_3F_4P$-PPV in the solid film consist of a multiple structured band comprising two maxima at around 535 and 566 nm, and the PL spectrum of P-$CF_3F_4P$-PPV in the solid film consist of a structured band comprising a maximum at around 542 nm. This indicate that $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV in thin film state have more red-shifted emission peaks than in solution condition by raising aggregation among polymer backbone, which can be attributed to the $\pi$-$\pi^*$ interaction between the conjugated main chains due to electron withdrawing effect of 2,3,5,6-tetrafluoro-4-trifluoromethylphenyl group.

**Table 3**. Electrochemical potentials and energy levels of the polymers

| polymer | $E_{ox}$[a] (V) | HOMO[b] (eV) | LUMO[c] (eV) | $E_g$[d] (eV) |
|---|---|---|---|---|
| $CF_3F_4P$-PPV | 0.70 | 5.50 | 3.14 | 2.36 |
| P-$CF_3F_4P$-PPV | 0.80 | 5.60 | 3.07 | 2.53 |

[a] Onset oxidation potential measured by cyclic voltammetry. [b] Calculated from the oxidation potentials. [HOMO = 4.8 + ($E_{ox}$ – $E_{Fc}$)]. [c] Calculated from the HOMO energy levels and $E_g$. [d] Energy band gap was estimated from the onset wavelength of the optical absorption.

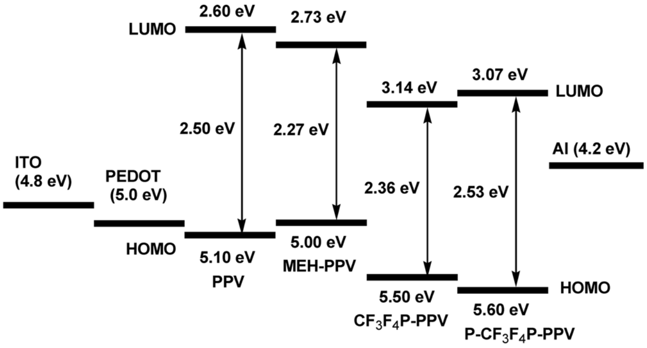


**Figure 3**. Energy band diagram of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV.

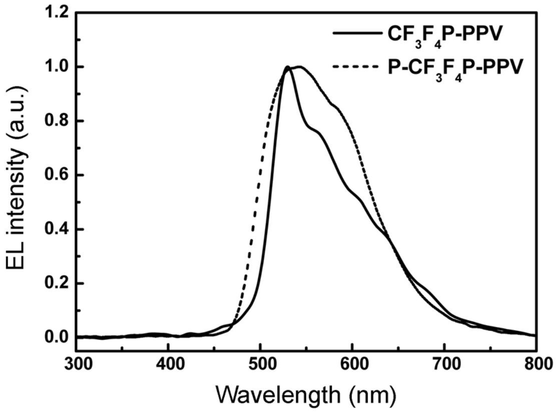


**Figure 4**. Electroluminescence spectra of PLEDs with the configuration of ITO/PEDOT/polymer/Al by using $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV.

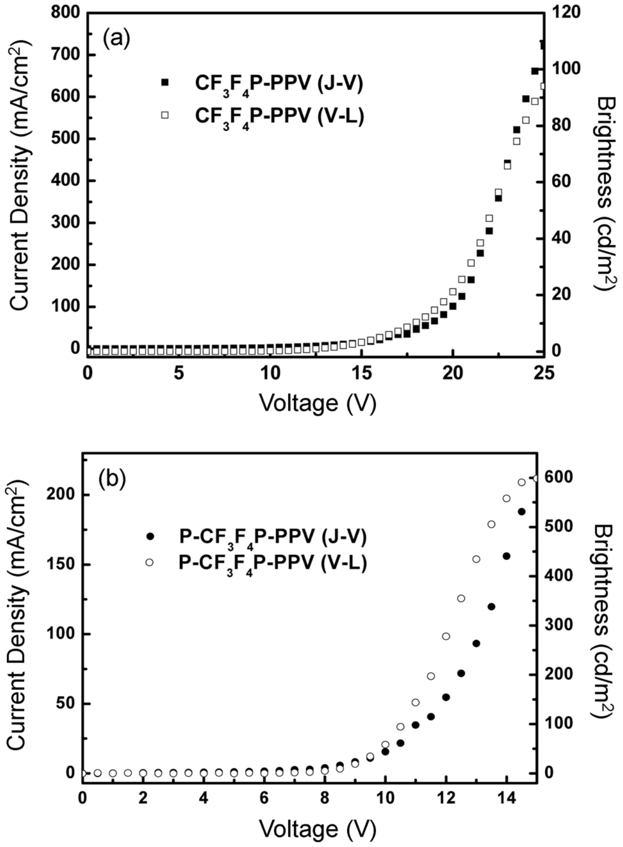


**Figure 5**. Current density-voltage-luminescence (*J-V-L*) characteristics of PLEDs with the configuration of ITO/PEDOT/polymer/Al by using $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV.

**Electrochemical Properties of the Polymers.** The energy band diagrams of polymers were determined from the band gaps which were estimated from the absorption edges, and the HOMO energy levels which were estimated from the cyclic voltammetry. All measurements were calibrated against an internal standard, ferrocene ($F_c$), which has the IP value (−4.8 eV) of the $F_c/F_c^+$ redox system. Electrochemical properties of the polymers were measured to show that all of the polymers exhibit irreversible processes in an oxidation scan. The oxidation onsets of the polymers were estimated to be 0.70 and 0.80 V for $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV, respectively, which correspond to HOMO energy level of 5.50 and 5.60 eV. The LUMO energy levels of polymers can be calculated with the HOMO and optical band gap. The LUMO energy levels of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV were thus determined to be 3.14 and 3.07 eV, respectively. The lower work function of the LUMO of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV as compared to that of PPV or MEH-PPV indicate that the electron injection process is easier in case of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV as compared to the case of PPV or MEH-PPV. Moreover, $CF_3F_4$phenyl group with the strong electron-withdrawing effects can lower more energy levels of HOMO and LUMO than other electron-withdrawing group.[23]

**Electroluminescent Properties and Current-Voltage-Luminance.** The electroluminescence (EL) spectra of ITO/PEDOT/polymer/Al devices is shown in Figure 4. The EL spectrum of $CF_3F_4P$-PPV is different in the PL spectrum which show two maximum peaks, by the way, the EL spectra of P-$CF_3F_4P$-PPV is nearly the same as the PL of the polymer. This result indicates that the EL and PL phenomena originated from the same excited state. The EL emission maxima of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV appear at around 530–543 nm. The emission colors of $CF_3F_4P$-

**Table 4**. Device performance characteristics of the polymers

| polymer | EL $\lambda_{max}$ (nm) | turn-on voltage[a] (V) | voltage[b] (V) | current density[b] ($mA/cm^2$) | luminance[c] ($cd/m^2$) | $LE_{max}$ [d] (cd/A) | CIE (*x,y*)[e] |
|---|---|---|---|---|---|---|---|
| $CF_3F_4P$-PPV | 530 | 12.5 | 17.5 | 34.8 | 82 | 0.025 | (0.41, 0.50) |
| P-$CF_3F_4P$-PPV | 543 | 7 | 12 | 54.7 | 598 | 0.51 | (0.42, 0.51) |

[a] Voltages required to achieve a brightness of 1 $cd/m^2$. [b] Measured under the condition of maximum luminescence efficiency. [c] Measured under the condition of maximum brightness. [d] Maximum luminescence efficiency. [e] Calculated from the EL spectrum.

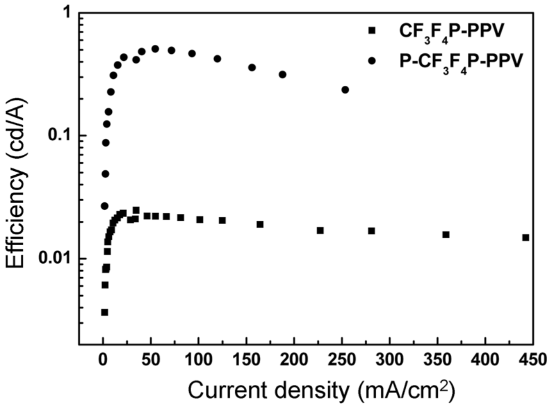


**Figure 6**. Current density-efficiency (cd/A) of PLEDs with the configuration of ITO/PEDOT/polymer/Al (b) by using $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV.

PPV and P-$CF_3F_4P$-PPV with the CIE coordinates of x = 0.41, y = 0.50 and x = 0.42, y = 0.51 yellow and orange.

The current density-voltage-luminescence (J-V-L) characteristics of ITO/PEDOT/polymer/Al devices are shown in Figure 5. In the forward bias, the turn-on voltage of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV are around 12.5 and 7.0 V, respectively, and the current densities increase in an exponential manner with increasing forward bias, which is typical of diode characteristic. The luminescence intensities of polymers are exponentially increased with an increase in voltage. The maximum luminescence ($L_{max}$) of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV are 82 and 598 cd/m$^2$. The low maximum brightness of the polymers could be attributed to the single layer device and poor morphology of the polymer films. As shown in Figure 6, the luminescence efficiencies of the polymers at room temperature are about 0.025-0.51 cd/A. As phenyl groups introduced in PPVs can increase the properties of polymers,[10] the maximum EL efficiency of P-$CF_3F_4P$-PPV (0.51 cd/A) with 2,3,5,6-tetrafluoro-4-trifluoromethylphenyl and alkoxy phenyl groups was higher than that of $CF_3F_4P$-PPV (0.025 cd/A) with 2,3,5,6-tetrafluoro-4-trifluoromethylphenyl and alkoxy groups.

## Conclusion

The research was focused at the syntheses of two new PPV derivatives, poly[2-(2-ethylhexyloxy)-5-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-1,4-phenylenevinylene] ($CF_3F_4P$-PPV), and poly[2-(4-(2-etylhexyloxy)-phenyl)-5-(2,3,5,6-tetrafluoro-4-trifluoromethylphenyl)-1,4-phenylenevinylene] (P-$CF_3F_4P$-PPV), which contain electron-withdrawing 2,3,5,6-tetrafluoro-4-trifluoromethylphenyl group, by Gilch polymerization. $M_n$, $M_w$, and PDI values of these polymers were in the range of 31000-52000, 157000-106000, 5.1-2.1, respectively. $T_d$ values of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV were measured to be 239 and 247 °C. The UV-visible absorption spectra of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV show the maximum peaks at 447-426 nm in THF solution, and 449-418 nm in solid thin film. The PL emission spectra in solid thin film are more red-shifted over 50 nm and increased fwhm than solution conditions by raising aggregation among polymer backbone, which can be attributed to the $\pi$-$\pi^*$ interaction between the conjugated main chains due to electron withdrawing effect of 2,3,5,6-tetrafluoro-4-trifluoromethylphenyl group. The EL emission maxima of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV appear at around 530-543 nm. The emission colors of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV with the CIE coordinates of x = 0.41, y = 0.50 and x = 0.42, y = 0.51 yellow and orange. As the result of the introduction of the electron-withdrawing $CF_3F_4$-phyenyl group to the phenyl backbone, the LUMO and HOMO energy levels of $CF_3F_4P$-PPV (3.14, 5.50 eV) and P-$CF_3F_4P$-PPV (3.07, 5.60 eV) were reduced. The current density-voltage-luminescence (J-V-L) characteristics of ITO/PEDOT/polymer/Al devices of $CF_3F_4P$-PPV and P-$CF_3F_4P$-PPV show that turn-on voltages are around 12.5 and 7.0 V, and the maximum brightness are about 82 and 598 cd/m$^2$, respectively. $CF_3F_4$phenyl group with the strong electron-withdrawing effects can lower more energy levels of HOMO and LUMO than other electron-withdrawing group, and as phenyl groups introduced in PPVs can increase the properties of polymers, the efficiency of P-$CF_3F_4P$-PPV (0.51 cd/A), which one more phenyl group was attached in polymer backbone with $CF_3F_4$phenyl group, is higher than $CF_3F_4P$-PPV (0.025 cd/A).

**Acknowledgements.** This work was supported by the Korea Research Foundation Grant Funded by the Korean Government (MOEHRD) (KRF-2005-042-C00087).

## References and Notes

1. Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737.
2. Suh, H.; Jin, Y.; Park, S. H.; Kim, D.; Kim, J.; Kim, C.; Kim, J. Y.; Lee, K. *Macromolecules* **2005**, *38*, 6285.
3. Huang, F.; Hou, L.; Wu, H.; Wang, X.; Shen, H.; Cao, W.; Yang, W.; Cao, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9845.
4. Peng, Q.; Peng, J. B.; Kang, E. T.; Neoh, K. G.; Cao, Y. *Macromolecules* **2005**, *38*, 7292.
5. Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934.
6. Jin, Y.; Kim, K.; Park, S. H.; Song, S.; Kim, J.; Jung, J.; Lee, K.; Suh, H. *Macromolecules* **2007**, *40*, 6799.
7. Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D. B.; Stoching, A. *Science* **1996**, *273*, 884.
8. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.
9. Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A.; Bredas, J. L.; Lõgdlund, M.; Salameck, W. R. *Nature (London)* **1999**, *357*, 121.
10. Jin, Y.; Kang, J. H.; Song, S.; Park, S. H.; Moon, J.; Woo, H. Y.; Lee, K.; Suh, H. *Bull. Korean Chem. Soc.* **2007**, *28*, 2419.
11. Jin, Y.; Kim, K.; Song, S.; Kim, J.; Kim, J.; Park, S. H.; Lee, K.; Suh, H. *Bull. Korean Chem. Soc.* **2006**, *27*, 1043.
12. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539.
13. Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.
14. Andersson, M. R.; Thomas, O.; Mammo, W.; Svensson, M.;

Theander, M.; Inganäs, O. *J. Mater. Chem.* **1999**, *9*, 1933.
15. Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
16. Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61*, 2793.
17. Parker, I. D.; Pei, Q.; Marrocco, M. *Appl. Phys. Lett.* **1994**, *65*, 1272.
18. Jin, Y.; Kim, J. Y.; Park, S. H.; Kim, J.; Lee, S.; Lee, K.; Suh, H *Polymer* **2005**, *46*, 12158.
19. Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature (London)* **1993**, *365*, 628.
20. Burn, P. L.; Grice, A. W.; Jajbakhsh, A.; Bradley, D. D. C.; Thomas, A. C. *Adv. Mater.* **1997**, *9*, 1171.
21. Bredas, J. L.; Heeger, A. J. *Chem. Phys. Lett.* **1994**, *54*, 401.
22. Ko, S. W.; Jung, B.-J.; Ahn, T.; Shim, H.-K. *Macromolecules* **2002**, *35*, 6217.
23. Jin, Y.; Kim, J.; Park, S. H.; Lee, K.; Suh, H. *Bull. Korean Chem. Soc.* **2005**, *26*, 795.
24. Sarnecki, G. J.; Friend, R. H.; Moratti, S. C. *Synth. Met.* **1995**, *69*, 545.
25. Gurge, R. M.; Sarker, A.; Laht, P. M.; Hu, B.; Karasz, F. E. *Macromolecules* **1996**, *29*, 4287.
26. Gurge, R. M.; Sarker, A.; Laht, P. M.; Hu, B.; Karasz, F. E. *Macromolecules* **1997**, *30*, 8286.
27. Jin, J. I.; Kim, J. C.; Shim, H. K. *Macromolecules* **1992**, *25*, 5519.
28. Benjamin, I.; Faraggi, E. Z.; Avny, Y.; Davidov, D.; Neumann, R. *Chem. Mater.* **1996**, *8*, 352.
29. Lahti, P. M.; Sarker, A.; Garay, R. O.; Lenz, R. W.; Karasz, F. E. *Polymer* **1994**, *35*, 1312.
30. Grimsdale, A. C.; Cacialli, F.; Gruner, J.; Lix, C.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met*. **1996**, *76*, 165.
31. Boardman, F. H.; Grice, A. W.; Ruther, M. G.; Sheldon, T. J.; Bradley, D. D. C.; Burn, P. L. *Macromolecules* **1999**, *32*, 111.
32. Bröms, P.; Fahlman, M.; Xing, K. Z.; Salaneck, W. R.; Dannetun, P.; Cornil, J.; dos Santos, D. A.; Brédas, J. L.; Moratti, S. C.; Holmes, A. B.; Friend, R. H. *Synth. Met.* **1994**, *67*, 93.
33. Jin, Y.; Kim, J.; Lee, S.; Kim, J. Y.; Park, S. H.; Lee, K.; Suh, H. *Macromolecules* **2004**, *37*, 6711.
34. Jin, Y.; Ju, J.; Kim, J.; Lee, S.; Kim, J. Y.; Park, S. H.; Son, S. M.; Jin, S. H.; Lee, K.; Suh, H. *Macromolecules* **2003**, *36*, 6970.
35. Jin, Y.; Kim, J.; Song, S.; Park, S. H.; Lee, K.; Suh, H. *Bull. Korean Chem. Soc.* **2005**, *26*, 855.
36. Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925.