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Articles

Increased Efficiencies of the Copolymers with Fluoro Groups in Vinylene Units

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ABSTRACT: New electroluminescent copolymers with fluoro groups in the vinylene unit, poly(9,9-di-hexylfluorene-2,7-vinylene-*co*-*p*-phenylenedifluorovinylene) (**PFVPDFV**), have been synthesized by the GILCH polymerization. The fluoro groups were introduced on vinylene units to increase the electron affinities of the copolymers. The **PFVPDFV**s exhibit absorption spectra with maximum peaks at 371−413 nm. The maximum absorption peak at 413 nm of **PFVPDFV1** was blue-shifted with a larger amount of the **PDFV**. In the PL spectra of **PFVPDFVs**, as the **PDFV** content increases up to 50% in the copolymer system, the fwhm was decreased by 4−38 nm as compared to **PFV**. The HOMO energy levels of the copolymers were about 5.25−5.50 eV, and the LUMO energy levels were about 2.67−2.97 eV. The polymer LEDs (ITO/PEDOT/polymer/Al) of **PFVPDFVs** showed emission with maximum peaks at around 472−538 nm. By adjusting the feed ratios of **PDFV** in the copolymers, it was possible to tune the emission colors from greenish yellow to orange depending on the obtained CIE coordinates. The luminescence efficiencies of the copolymers at room temperature are about 0.1−1.47 cd/A. **PFVPDFV3** showed the maximum brightness of 4870 cd/m^2 and the highest luminescence efficiency of 1.47 cd/A. The introduction of up to 50% of **PDFV** in **PFVPDFVS** can enhance the device performance to result in high current density, brightness, and efficiency due to the increased electron injection ability caused by the presence of fluoro groups in the vinylene units.

Introduction

For use in full color flat panel displays, one of the most promising candidates is a organic light-emitting diode (OLED), which has several advantages over conventional devices such as a low driving voltage, wide viewing angle, thin film structure, and a simpler manufacturing process.[1] Numerous reports about polymer light-emitting diodes (PLEDs) have been published since the discovery of electroluminescence (EL) from conjugated polymers.[2−4] Most of the research in the field of polymer-based electroluminescent devices has been focused on main-chain conducting polymers such as poly(phenylenevinylene) (PPV),[5] poly(*p*-phenylene) (PPP),[6] poly(thiophene),[7] poly(fluorene),[8] and their copolymers and soluble derivatives, because of their prospective application as large-area light emitting diodes (LEDs).[9−13]

PPV and its derivatives have attracted much attention, and a large number of studies have been reported. The synthesis of these polymers by Gilch polymerization increased the possibility of employing this promising class of polymers for LEDs. Due to the presence of vinylene units, PPV derivatives exhibit emissions of longer wavelength as compared to the case of PF or PPP without vinylene units. There are several examples of PPVs which show high efficiencies, long lifetimes, and emissions of red to green colors in LEDs.[14,15]

PF derivatives were introduced as blue-light emitting materials with relatively large band gaps.[16,17] To cover the whole range of visible light, several types of copolymers of fluorene were synthesized to control the emission wavelength and band gap. Vinylene units have been introduced in PF to generate poly(fluorenevinylene)s (PFVs, Chart 1) which showed red-shifted emission as compared to PFs.[18,19]

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.[20,21] The application of additional organic charge-transporting layers between the emissive layer and the electrodes or adjustment of the energy band of the polymer by introduction of electron-withdrawing groups attached to the polymer backbone have been tried for the improvement of the properties 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

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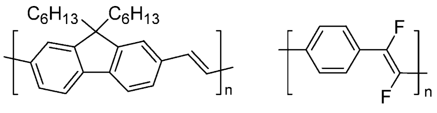
Chart 1



PFV **PPDFV**

rings or the vinylene groups of the polymer.[22] The electron-withdrawing substituents such as halide,[23,24] cyano,[25] trifluoromethyl,[26] or (methylsulfonyl)phenyl[27] were introduced on the arylene rings of PPV derivatives. Several conjugated polymers with cyano or fluoro groups on vinylene units have also been reported.[28−30]

The present investigation deals with the synthesis, characterization, photophysics, and electroluminescence (EL) of new copolymers, poly(dihexylfluorenevinylene)-*co*-poly(*p*-phenylenedifluorovinylene)s (**PFVPDFVs**). We previously reported the synthesis and electroluminescence properties of new EL polymers, poly(*p*-phenylenedifluorovinylene) (**PPDFV**, Chart 1) and poly(2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (**DMOS−PPDFV**),[30] which contain two fluoro groups in every vinylene unit to reduce the barrier of electron injection. The new copolymers, **PFVPDFVs**, containing dihexylfluorenevinylene (**PFV**), and phenylenedifluorovinylene (**PDFV**), were synthesized by Gilch polymerization.[31,32] Synthesized **PFVPDFV**s were incorporated with **PDFV**, having two fluoro groups in a vinylene unit, to investigate the effect of the electron-withdrawing fluorine atom on the optical and device properties of the copolymers.

Experimental Section

Materials and Instruments. All reagents used 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), Unityplus-300 (300 MHz) and Inova-500 (500 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 aluminum 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. For the EL experiment, 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. An isopropyl solution of the PEDOT/PSS was spin-coated on the surface-treated ITO substrate. On top of the PEDOT/PSS 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 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. To examine electrochemical properties of the resulting polymer, the polymer film was cast from THF solution onto a platinum plate as a working electrode. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s. Elemental analysis (Korea Basic Science Institute: Daegu) was observed toward identification of the structure of polymers. FAB Mass spectra was determined using at Korea Basic Science Institute Seoul Branch and Korea Basic Science Institute Daegu Branch.

2,7-Dibromo-9,9′-dihexyl-9*H*-fluorene (1). To a stirred solution of 5 g (15.43 mmol) of 2,7-dibromo-9*H*-fluorene in 40 mL of DMSO under argon was added catalytic amounts of triethylbenzylammonium chloride. After 1 h at 60 °C, 6.37 g (38.60 mmol) of *n*-bromohexane was added to the reaction mixture. After an additional 1 h at 60 °C, the mixture was treated with 25 mL of 50% aqueous NaOH, stirred for 5 h at room temperature, and diluted with 500 mL of ethyl acetate. The organic layer was washed with 100 mL of a 1.0 M hydrochloric acid solution, and 150 mL of water. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure. The oily residue was purified by flash column chromatography (30 × 150 mm column, SiO_2, 100% of hexane) to give 7.22 g (95.0%) of 2,7-dibromo-9,9′-dihexyl-9*H*-fluorene (**1**), white crystals: mp 61 °C, R_f 0.57 (SiO_2, hexane 100%).

^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.45−0.68 (m, 4H), 0.77 (t, 6H $J = 6.6$ Hz), 0.90−1.20 (m, 12H), 1.86−1.95 (m, 4H), 7.43−7.54 (m, 6H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 13.98, 22.57, 23.63, 29.56, 31.45, 40.18, 55.66, 121.11, 121.45, 126.15, 130.13, 139.04, 152.53.

9,9′-Dihexyl-9*H*-fluorene-2,7-dicarbaldehyde (2). To a stirred solution of 5.0 g (10.2 mmol) of dihexyl compound **1** in 20 mL of THF at −78 °C under argon was slowly added 14.0 mL (22.3 mmol) of *n*-BuLi (1.60 M in hexane solution). After 30 min, the reaction mixture was slowly treated with 10.3 mL (102 mmol) of formylmorpholine at −78 °C. After stirring at room temperature for 24 h, the reaction was quenched with 80 mL of 0.1 M HCl. The organic phase was separated and the aqueous phase was extracted several times with methylene chloride. The combined organic phase was treated with dried $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (40 × 220 mm column, SiO_2, ethyl acetate:hexane = 1:20) to give 2.7 g (67.8%) of 9,9′-dihexyl-9*H*-fluorene-2,7-dicarboxylate (**2**), a yellow solid. R_f 0.4 (SiO_2, ethyl acetate:hexane = 1:5).

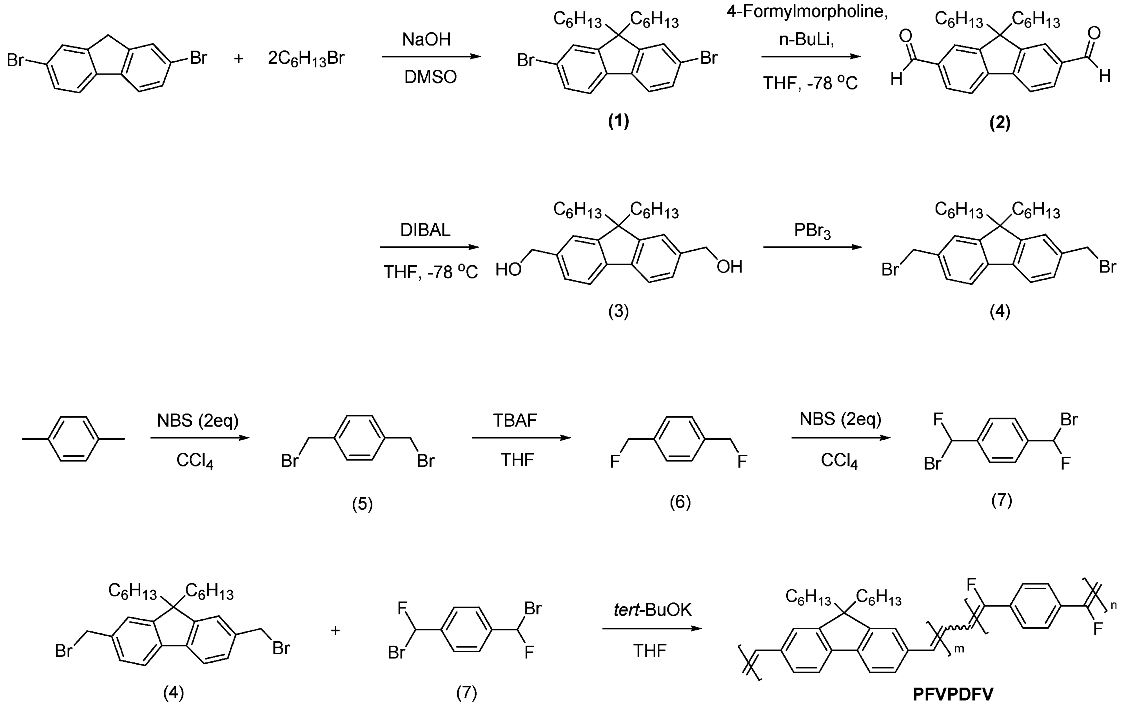
^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.40−0.64 (m, 4H), 0.74 (t, 6H $J = 6.6$ Hz), 0.80−1.20 (m, 12H), 2.03−2.12 (m, 4H), 7.92 (s, 6H), 10.11 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 13.91, 22.47, 23.74, 29.47, 31.40, 40.02, 55.56, 121.30, 123.34, 130.31, 136.39, 145.59, 152.84, 192.19.

(9,9′-Dihexyl-7-hydroxymethyl-9*H*-fluorene-2-yl)methanol (3). To a stirred solution of 2.7 g (6.92 mmol) of dicarbaldehyde compound **2** in 10 mL of THF at −78 °C under argon was added 34.6 mL (34.6 mmol) of 1.0 M solution of diisobutylaluminum hydride in THF. After 2 h at −78 °C, the reaction mixture was cautiously treated with 3 mL of methanol, warmed to room temperature, and diluted with 100 mL of diethyl ether. The reaction mixture was washed with 10 mL of a saturated aqueous sodium chloride solution. The total aqueous layer was washed with 2 × 50 mL of ether. The combined organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The oily residue was purified by flash chromatography (40 × 180 mm column, SiO_2, ethyl acetate:hexane = 1:9) to give 2.6 g (95%) of (9,9′-dihexyl-7-hydroxymethyl-9*H*-fluorene-2-yl)methanol (**3**), a yellow oil: R_f 0.13 (SiO_2, ethyl acetate:hexane = 1:4).

^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.45−0.68 (m, 4H), 0.78 (t, 6H $J = 6.6$ Hz), 0.90−1.20 (m, 12H), 1.69 (s, 2H), 1.90−1.98 (m, 4H), 4.77 (s, 4H), 7.31 (d, 4H, $J = 7.6$ Hz), 7.66 (d, 2H, $J = 8.4$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 13.91, 22.51, 23.68, 29.63, 31.42, 40.28, 54.93, 65.53, 119.56, 121.44, 125.69, 139.71, 140.28, 151.22.

2,7-Bis(bromomethyl)-9,9′-dihexyl-9*H*-fluorene (4). To a stirred solution of 2.18 g (5.52 mmol) of diol compound **3** in 20 mL of benzene at 0 °C under argon was added, drop by drop, 1.57 mL

Scheme 1. Synthetic Routes for the Monomers and the Polymers



(16.57 mmol) of PBr_3. The reaction mixture was stirred at 45 °C for 6 h, cooled, and diluted with 5 mL of water. The aqueous layer was separated and extracted with $CHCl_3$. The total aqueous layer was washed with 2 × 10 mL of $CHCl_3$, and the combined organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The oily residue was purified by flash chromatography (40 × 150 mm column, SiO_2, 100% hexane) to give 2.79 g (97%) of 2,7-bis(bromomethyl)-9,9′-dihexyl-9*H*-fluorene (**4**), colorless oil: R_f 0.35 (SiO_2, ethyl acetate:hexane = 1:8).

^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.45−0.68 (m, 4H), 0.78 (t, 6H $J = 6.6$ Hz), 0.90−1.20 (m, 12H), 1.89−1.98 (m, 4H), 4.60 (s, 4H), 7.34 (d, 4H, $J = 2.2$ Hz), 7.64 (d, 2H, $J = 8.0$ Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 13.99, 22.48, 23.62, 29.53, 31.35, 34.47, 40.07, 55.12, 120.04, 123.64, 127.99, 136.86, 140.72, 151.63. HRMS (EI): *m*/*z* 518.1179 (calculated for $C_{27}H_{36}Br_2$ 518.1184). Anal. Calcd for $C_{27}H_{36}Br_2$: C, 62.32; H, 6.97. Found: C, 62.10; H, 7.01.

α,α′-Dibromo-*p*-xylene (5). The reaction mixture of 6 g (56.51 mmol) of *p*-xylene and 20.1 g (113.2 mmol) of *N*-bromosuccinimide (NBS) in 50 mL of CCl_4 at room temperature under argon was irradiated with light source (300 W) for 1 h. After filtering, the filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (40 × 150 mm column, SiO_2, 100% hexane) to give 9.9 g (67%) of α,α′-dibromo-*p*-xylene (**5**), a white solid: R_f 0.25 (SiO_2, hexane 100%).

^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 4.48 (s, 4H), 7.37 (s, 4H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 32.75, 129.40, 137.94.

α,α′-Difluoro-*p*-xylene (6). To a stirred solution of 10 g (37.88 mmol) of dibromo-*p*-xylene (**5**) in 20 mL of tetrahydrofuran (THF) at room temperature, was added 98.5 mL (98.5 mmol) of 1.0 M TBAF (tetrabutylammonium fluoride) in THF. After stirring for 24 h at 50 °C, the reaction mixture was concentrated in vacuo to remove the solvent. After adding hexane, the mixture was stirred for 1 h, and filtered. The filtrate was concentrated in vacuo and purified by column chromatography to give 2.3 g (42.9%) of the desired α,α′-difluoro-*p*-xylene (**6**), yellow oil: R_f 0.28 (60 × 180 mm column, SiO_2, Hexane 100%).

^{1}H NMR (200 MHz, acetone-d_6): δ (ppm) 5.43 (d, 4H, $J = 49.4$ Hz), 7.47 (s, 4H). ^{13}C NMR (50 MHz, acetone-d_6): δ (ppm) 84.90 (d, $J = 163.5$ Hz), 128.80 (d, $J = 6.5$ Hz), 138.13 (d, $J = 20$ Hz).

1,4-Bis(bromofluoromethyl)benzene (7). A stirred mixture of 716 mg (5.04 mmol) of difluoromethyl compound **6** and 1.79 g (10.07 mmol) of NBS in CCl_4 (20 mL)at room temperature was irradiated with the light source (300 W) for 1 h. The reaction mixture was filtered in order to remove generated succinimide. The filtrate was concentrated in vacuo and purified by flash column chromatography (15 × 150 mm column, SiO_2, 100% of hexane) to give 688 mg (45.5%) of the desired 1,4-bis(bromofluoromethyl)-benzene (**7**), white solid: R_f 0.20 (SiO_2, hexane 100%).

^{1}H NMR (200 MHz, acetone-d_6): δ (ppm) 7.86 (d, 2H, $J = 48$ Hz), 7.72 (s, 4H). ^{13}C NMR (50 MHz, acetone-d_6): δ (ppm) 92.74 (d, $J = 249.5$ Hz), 126.63 (d, $J = 6.5$ Hz), 141.94 (d, $J = 20$ Hz). HRMS (EI): *m*/*z* 297.8808 (calculated for $C_8H_6Br_2F_2$ 297.8804). Anal. Calcd for $C_8H_6Br_2F_2$: C, 32.04; H, 2.02. Found: C, 32.10; H, 1.94.

Poly(dihexylfluorenevinylene)-*co*-poly(*p*-phenylenedifluorovinylene) (PFVPDFV) (8). PFVPDFVs with various feed ratios of **PFV** and **PDFV** contents were synthesized. To a stirred solution of monomer **4** and **7** (total amount of 1.5 mmol) in 20 mL of THF at 40 °C under argon was added 36 mL (9.0 mmol) of a 0.25 M solution of potassium *tert*-butoxide in THF by a syringe pump over 1 h. Over the addition, the reaction mixture had a color change from colorless via greenish to yellow, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred for 10 h at room temperature. The reaction mixture was slowly poured into 200 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with water, and dried under reduced pressure at room temperature to generate the crude polymer as a yellow powder. The resulting polymer was redissolved in 100 mL of THF at 60 °C, cooled to 40 °C, and reprecipitated by dropwise addition of 500 mL of methanol. The precipitated polymer was filtered and dried at room temperature under reduced pressure. This procedure was repeated once more using 100 mL of THF/1.0 L of methanol to generate **PFVPDFVs** (**PFVPDFV1** (copolymer with 10 mol % **PDFV** in the feed), **PFVPDFV3** (copolymer with 30 mol % **PDFV** in the feed), **PFVPDFV5** (copolymer with 50 mol % **PDFV** in the feed), **PFVPDFV7** (copolymer with 70 mol % PDFV in the feed) and **PFVPDFV9** (copolymer with 90 mol % **PDFV** in the feed)). The polymer fibers had colors ranging from sky blue to light yellow. The yields of the polymers were from 19 to 54%.

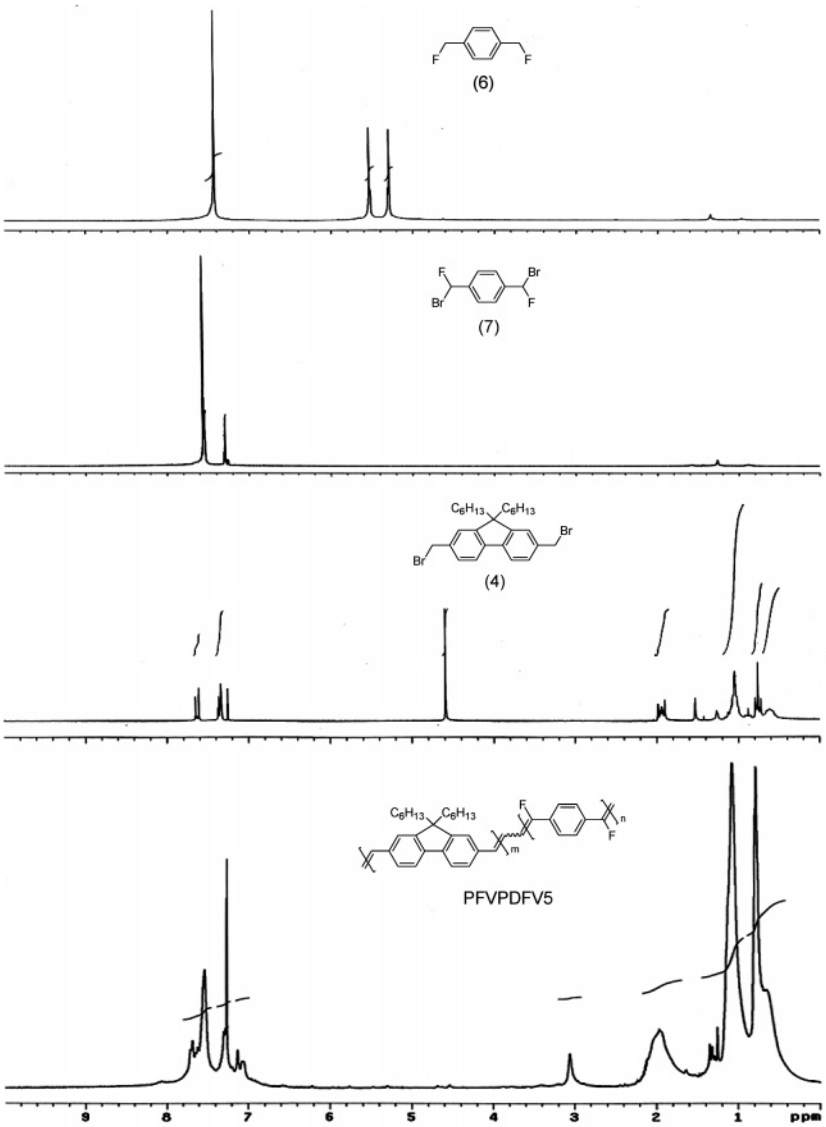


Figure 1. ^{1}H NMR spectra of α,α′-difluoro-*p*-xylene (a), the monomers (b, c), and **PFVPDFV5** (d) in $CDCl_3$.

Results and Discussion

Synthesis and Characterization of Polymers. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. By the previously reported method, various feed ratios of monomers **4** and **7** were used for the preparation of **PFVPDFV**s by the Gilch reaction.[19,30] Figure 1 shows the ^{1}H NMR spectra of an intermediate (α,α′-difluoro-*p*-xylene (**6**) (a), monomer **7** (b), monomer **4** (c), and **PFVPDFV5** (d) in $CDCl_3$. The shift from the characteristic fluoromethyl proton peak at 5.43 (d, 4H, $J = 49.4$ Hz) ppm of fluoromethyl compound to the bromofluoromethyl proton peak at 7.86 (d, 2H, $J = 48$ Hz) ppm of the monomer **7** confirms the synthesis of the monomer unit which could be polymerized to generate the polymer with fluoro groups in vinylene units by Gilch polymerization reaction. The absence of the characteristic bromomethyl proton peak at 4.60 ppm and bromofluoromethyl proton peak at 7.86 ppm of the monomers confirms the polymerization, and all other peaks are in good agreement with the structure of the polymer. A defect structure revealed by the peak at 3.0 ppm representing head-to-head formation instead of regular head-to-tail formation was detected in Gilch polymerized **PFVPDFV**,[18,33] and the amount of defect was estimated to be about 10%.

Table 1 summarizes the polymerization results including molecular weights, PDI, and thermal stability of the copolymers. These copolymers have weight-average molecular weight (M_w) of 4000−21 000 with PDI (poly dispersity index, M_w/M_n) of 1.60−2.49. The thermal properties of the copolymers were determined by TGA measurements. All these copolymers show good thermal stability, with onset decomposition temperature (T_d, 5% weight loss) of 300−430 °C under nitrogen.

Table 1. Characterization of the PFVPDFVs

polymer	yield (%)	$M_w{}^a$ ($\times 10^3$)	PDI[a]	$T_d{}^b$ (°C)
PFVPDFV1	54	21	1.85	430
PFVPDFV3	46	22	2.09	410
PFVPDFV5	50	34	2.49	385
PFVPDFV7	45	31	2.37	340
PFVPDFV9	19	6.3	1.47	300

[a] Molecular weight (M_w) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. [b] Onset decomposition temperature (5% weight loss) measured by TGA under N_2.

Optical Properties. Figure 2 shows the absorption and photoluminescence (PL) spectra for **PFV**, **PFVPDFV5**, and **PPDFV** in different solvents which are summarized in Table 2. In organic solvents such as DMF, THF, toluene, and chlorobenzene, the polymers display maxima and peak shapes that are typical for this type of polymer. Absorption and emission spectra of **PFVPDFV5** are similar to those of **PFV** in THF,

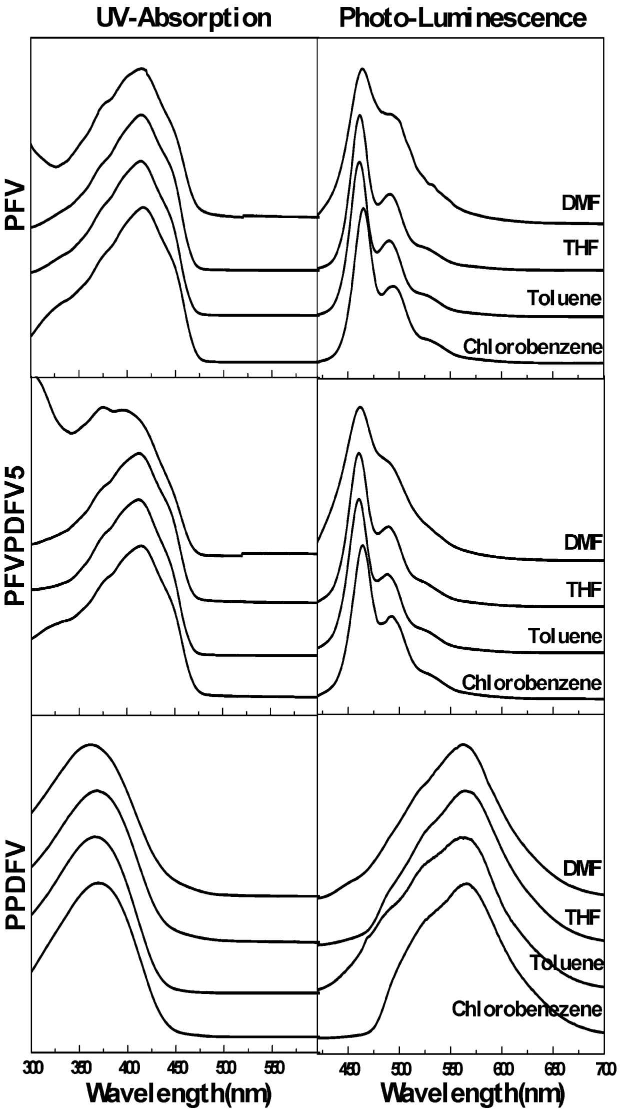


Figure 2. UV−vis absorption and photoluminescence spectra of **PFV, PFVPDFV**, and **PPDFV** in the DMF, THF, toluene, and chlorobenzene solutions.

toluene, and chlorobenzene. In the case of polar DMF as the solvent, the possible interaction between DMF and polar fluoro groups caused a hypochromic shift in absorption. The PL spectra of **PPDFV** is very much red-shifted, as compared to the case of **PFVPDFV5**, caused by the aggregation.

Transparent and uniform copolymer films were prepared on quartz plates by spin-casting from their respective chlorobenzene solution at room temperature. The absorption and emission data for the copolymers are summarized in Table 3. As shown in Figure 3, there is not much difference between the absorption spectra of the solutions and the thin films of the copolymers, which can be attributed to the $\pi-\pi^*$ transitions of the copolymers. The **PFVPDFV**s exhibit absorption spectra with maximum peaks at 371−413 nm. The maximum absorption peak at 413 nm of **PFVPDFV1** was blue-shifted with more amount of the **PDFV**. This is originated from the decrease of the electron density along the π-conjugated polymer backbone by incorporation of the **PDFV** segment and decrease of the effective conjugation length of the copolymers.

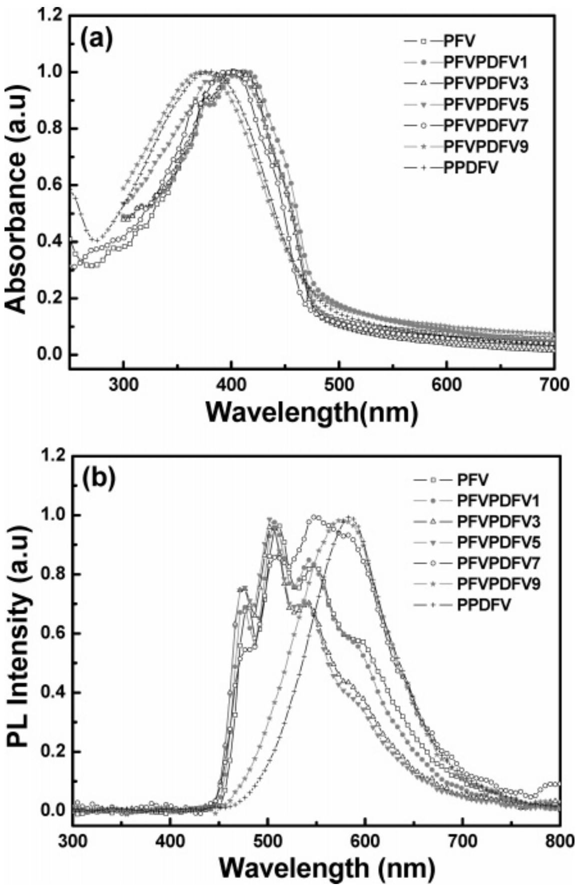


Figure 3. UV−vis absorption (a) and photoluminescence (b) spectra of **PFVPDFV**s in the solid state.

The PL spectra of the **PFVPDFV**s in thin film show maxima around 502−572 nm. In the case of **PFVPDFV1**, **PFVPDFV3**, and P**FVPDFV5** in thin film, the $S_1 \rightarrow S_0$ 0−1 transitions exhibit emission maxima at around 505 nm, and the vibronic features of the $S_1 \rightarrow S_0$ 0−0 and 0−2 transitions are presented at 477 and 542 nm. Although the emission peaks of these polymers are similar, as the **PDFV** content was increased up to 50% in the copolymer system, the full width at half-maximum (fwhm) was decreased by 4−38 nm as compared to **PFV**. The effects of blue-shifted absorption peak and red-shifted emission peak of **PPDFV** appear also in **PFVPDFV7** and **PFVPDFV9** which possess higher proportion of **PDFV** than **PFV**. In the case of **PFVPDFV7**, the peak at 582 nm is increased by the effect of **PDFV**, and in the case of **PFVPDFV9**, this peak is dominant, to yield an emission spectrum similar to that of **PPDFV**.

Electrochemical Properties. The electrochemical properties of the copolymers 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 (CV). The CV was performed with a solution of

Table 2. Optical Properties in Different Solvents

	abs λ_{max} (nm)				PL λ_{max} (nm)			
polymer	DMF	THF	toluene	chlorobenzene	DMF	THF	toluene	chlorobenzene
PFV	414	415	414	417	464	461	461	465
PFVPDFV5	375 397	413	412	415	464	461	461	464
PPDFV	361	368	366	370	563	563	559	565

Table 3. Characteristics of the UV−Vis Absorption, Photoluminescence, and Electroluminescence Spectra

feed ratio of copolymers	abs λ_{max} (nm)	PL λ_{max}[a] (nm)	fwhm[b] of PL	EL λ_{max}[a] (nm)	fwhm[b] of EL
PFV	412	512 (481, 547, 598)	137	508 (477, 543)	133
PFVPDFV1	413	507 (477, 542, 592)	133	503 (472, 538)	120
PFVPDFV3	401	502 (477, 542, 587)	104	508 (472, 538)	99
PFVPDFV5	397	502 (477, 542, 587)	99	498 (472, 538)	81
PFVPDFV7	402	547 (477, 502, 582)	158	472, 498 (538)	101
PFVPDFV9	371	572	114	538	120
PPDFV	376	583	99	558	125

[a] The data in the parentheses are the wavelengths of shoulders and subpeaks. [b] Full width at half-maximum of PL and EL spectra.

Table 4. Electrochemical Potentials and Energy Levels of the Copolymers

feed ratio of copolymers	E_{onset}[a] (V)	HOMO[b] (eV)	LUMO[c] (eV)	E_g[d] (eV)
PFV	0.65	−5.30	−2.70	2.60
PFVPDFV1	0.60	−5.25	−2.67	2.58
PFVPDFV3	0.60	−5.25	−2.69	2.56
PFVPDFV5	0.70	−5.35	−2.79	2.56
PFVPDFV7	0.65	−5.30	−2.76	2.54
PFVPDFV9	0.85	−5.50	−2.97	2.53
PPDFV	0.85	−5.50	−3.02	2.48

[a] Onset oxidation potential measured by cyclic voltammetry. [b] Calculated from the oxidation potentials. [c] Calculated from the HOMO energy levels and E_g. [d] Energy band gap was estimated from the onset wavelength of the optical absorption.

tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under the protection of argon. A platinum electrode (~0.05 cm^2) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO$_3$ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO$_3$ reference electrode (calibrated by the FC/FC+ redox system) was 4.65 eV below the vacuum level. The oxidation potentials derived from the onset of electrochemical p-doping are summarized in Table 4. HOMO levels were calculated according to the empirical formula ($E_{HOMO} = -([E_{onset}]^{ox} + 4.65)$ (eV).[34,35] During the anodic scan, the oxidation onset potentials of **PFVPDFV**s are in the range 0.60−0.85 V, and exhibited an irreversible p-doping process. HOMO energy levels of the present copolymers are about 5.25 − 5.50 eV. In the case of **PFVPDFV9**, the HOMO energy level was the most decreased, which is caused by the electron-withdrawing effect of the fluoro group. The absorption onset wavelengths of **PFVPDFV**s were 490−580 nm, which correspond to band gaps of 2.53−2.58 eV. The LUMO energy level was calculated from the values of the band gap and HOMO energy level, and the values are about 2.67− 2.97 eV.

Electroluminescent Properties and Current Density—Voltage—Luminescence (*J*—*V*—*L*) Characteristics. The electroluminescence (EL) spectra of ITO/PEDOT/polymer/Al devices are shown in Figure 4. The EL spectra of the polymers are nearly the same as the PL of the polymers. This result indicates that the EL and PL phenomena originated from the same excited state. In the case of **PFVPDFV1**, **PFVPDFV3**, and **PFVPDFV5**, the emission maxima appear around 498−508 nm. As the **PDFV** content increase up to 50% in the copolymer system, the fwhm was decreased by 13−52 nm as compared to **PFV**. **PFVPDFV7** exhibits maximum peaks at 472 and 498 nm, and **PFVPDFV9** exhibits maximum emission at around 538 nm. With higher ratio of **PDFV** contents, the shoulder peak of **PFV** in around 540 nm was being changed and became the maximum peak in **PFVPDFV9**.

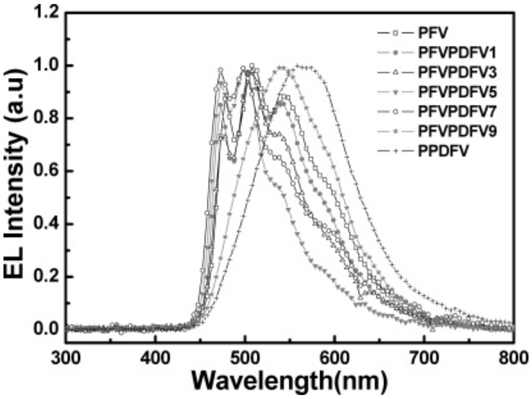


Figure 4. Electroluminescence spectra of devices with the configuration of ITO/PEDOT/copolymers/Al.

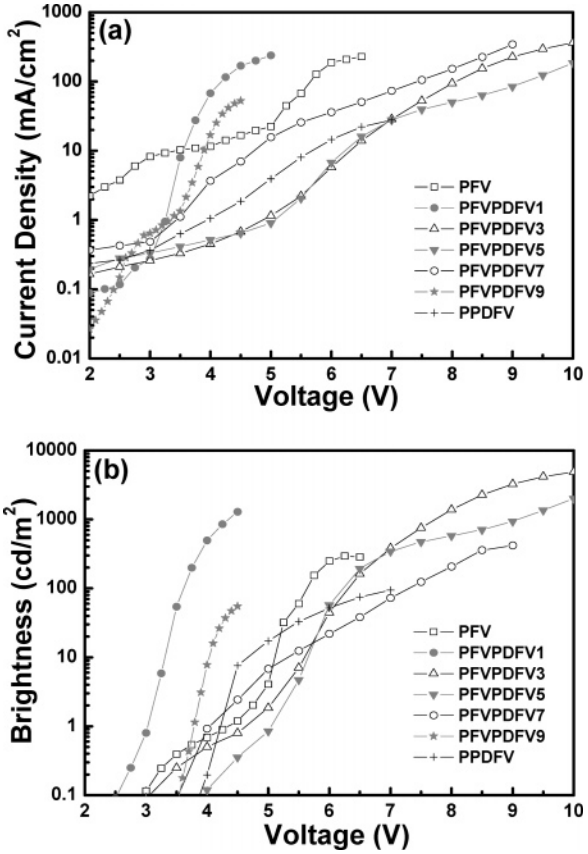


Figure 5. (a) Current−voltage (*I*−*V*) and (b) voltage−luminescence (*V*−*L*) characteristics of OLEDs of **PFVPDFV**s with the configuration of ITO/PEDOT/copolymers/Al.

The current density−voltage (*J*−*V*) and luminescence−voltage (*L*−*V*) characteristics of ITO/PEDOT/polymer/Al devices are shown in Figure 5. The copolymers with higher **PDFV** contents can have higher current density due to increasing electron injection ability by the low electron density, which is caused by the presence of fluoro groups in vinylene units. However, **PFVPDFV5** shows the highest current density,

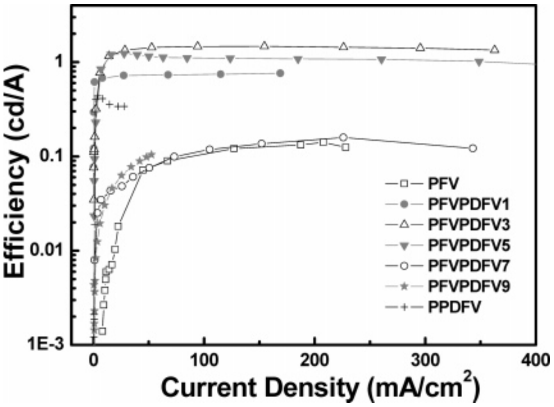


Figure 6. Efficiencies of OLEDs of **PFVPDFV**s with the configuration of ITO/PEDOT/copolymers/Al.

Table 5. Device Performance Characteristics of PFVPDFVs

feed ratio of copolymers	turn-on voltage[a] (V)	voltage[b] (V)	current density[b] (mA/cm^2)	luminance[b] (cd/m^2)	LE$_{max}$[c] (cd/A)	CIE (*x*, *y*)[d]
PFV	4.5	6.5	207	293	0.14	(0.32, 0.44)
PFVPDFV1	3.25	4.5	169	1286	0.76	(0.29, 0.42)
PFVPDFV3	5	10	363	4870	1.47	(0.28, 0.42)
PFVPDFV5	5.5	12	496	4084	1.23	(0.22, 0.34)
PFVPDFV7	4	9	343	418	0.16	(0.26, 0.34)
PFVPDFV9	3.8	4.5	53	55	0.10	(0.37, 0.48)
PPDFV	4	7	27	94	0.47	(0.43, 0.49)

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

because this polymer has good solubility and low electron density with a high percentage of the fluoro-substituted vinylene unit. **PFVPDFV9** showed the lowest current, since the interaction between the polymers is not good, which was caused by the low solubility in organic solvents. The turn-on voltages of ITO/PEDOT/polymer/Al devices are about 3.25−5.5 V. The luminescence intensities of the polymers are increased with an increase in voltage. The maximum luminescence (L_{max}) of **PFVPDFV3** is 4870 cd/m^2 at 10 V.

The emission colors of **PFV** and **PPDFV** with the CIE coordinates of $x = 0.32$, $y = 0.44$ and $x = 0.43$, $y = 0.49$ are greenish yellow and orange. By adjusting the feed ratios of **PDFV** in **PFVPDFV**s, it was possible to tune the emission colors from greenish yellow to orange depending on the obtained CIE coordinates. As shown in Figure 6, the luminescence efficiencies of the copolymers at room temperature are about 0.1−1.47 cd/A. **PPDFV** was reported by us as a polymer with high efficiency caused by the high electron injection ability,[30] which was originated by the presence of fluoro group on vinylene unit, but low solubility is still problematic. For the same reason, the increase of **PDFV** contents in **PFVPDFVs** can get both merit and demerit. **PFVPDFV1**, **PFVPDFV3**, and **PFVPDFV5**, which have the merit of improved electron injection ability by increasing **PDFV** portion, show high efficiencies. **PFVPDFV7** and **PFVPDFV9**, which have the demerit of low solubility in organic solvents, show low efficiencies. Therefore, we conclude that the introduction of up to 50% of **PDFV** in **PFV** can enhance the device performance to result in low fwhm of PL and EL spectra and high current density, brightness and efficiency.

Conclusion

Copolymers with difluoro groups in vinylene unit, **PFVPDFVs**, were synthesized by the Gilch reaction. The **PFVPDFV**s exhibit absorption spectra with maximum peaks at 371−413 nm. The maximum absorption peak at 413 nm of **PFVPDFV1** was blue-shifted with more amount of the **PDFV**. This is originated from the decrease of the electron density along the π-conjugated polymer backbone by incorporation of the **PDFV** segment and decrease of the effective conjugation length of the copolymers. In the PL spectra of **PFVPDFV1**, **PFVPDFV3**, and P**FVPDFV5** in thin film, the $S_1 \rightarrow S_0$ 0−1 transitions exhibit emission maxima at around 505 nm. As the **PDFV** content was increased up to 50% in the copolymer system, fwhm was decreased by 4−38 nm as compared to **PFV**. In the case of **PFVPDFV7**, the peak at 582 is increased by the effect of **PDFV**, and in the case of **PFVPDFV9**, this peak is dominant to make emission spectrum similar to that of **PPDFV**. The HOMO energy levels of the copolymers were about 5.25−5.50 eV, and the LUMO energy levels were about 2.67−2.97 eV.

The polymer LEDs of **PFVPDFVs** with the configuration of ITO/PEDOT/polymer/Al emitted light with maximum peaks at around 472−538 nm. By adjusting the feed ratios of **PDFV** in the copolymers, it was possible to tune the emission colors from greenish yellow to orange depending on the obtained CIE coordinates. The luminescence efficiencies of the copolymers at room temperature are about 0.1−1.47 cd/A. **PFVPDFV3** showed the maximum brightness of 4870 cd/m^2 and the highest luminescence efficiency of 1.47 cd/A. In conclusion, the introduction of up to 50% of **PDFV** in **PFVPDFVS** can enhance the device performance (Table 5) to result in high current density, brightness and efficiency due to the increased electron injection ability caused by the presence of fluoro groups in the vinylene units.

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