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Synthesis and electroluminescent properties of copolymers based on PPV with fluoro groups in vinylene units

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Abstract

New electroluminescent copolymers with fluoro groups in vinylene unit, poly(2-ethylhexyloxy-5-methoxy-*p*-phenylenevinylene-*co*-2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (MEH-PPV-*co*-DMOS-PPDFV) and poly(2-dimethyloctylsilyl-*p*-phenylenevinylene-*co*-2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (DMOS-PPV-*co*-DMOS-PPDFV), have been synthesized by the Gilch polymerization. The fluoro groups were introduced on vinylene units to increase the electron affinity of the copolymers. In both types of the copolymers, the band gaps were increasing with higher ratio of DMOS−PPDFV. As compared to the PL spectra in solution state, PL spectra in solid state and EL spectra of both types of copolymers showed red shifted and broad peaks caused by the aggregation. The polymer LEDs of MEH-PPV-*co*-DMOS-PPDFVs emit light with maximum peaks at around 538−577 nm. By adjusting the feed ratios of DMOS−PPDFV in the copolymers, we could tune the emission colors from orange yellow to green. DMOS-PPV-*co*-DMOS-PPDFVs showed the maximum EL peaks at about 514−543 nm. DMOS-PPV-*co*-DMOS-PPDFV with 1:9 feed ratio showed the highest luminescence efficiency of 1.31 lm/W.

Keywords: Light-emitting diodes; PPV; Efficiency

1. Introduction

Caused by the prospective applications, numerous reports about polymer light-emitting diodes (PLEDs) have been published since the discovery of electroluminescence (EL) from conjugated polymers [1−4]. 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) [4], poly(*p*-phenylene) (PPP) [5], poly(thiophene) [6], poly(fluorene) [7], their copolymers and soluble derivatives, because of the prospective application as large-area light-emitting diodes (LEDs) [8−13].

It has been known that recombination of electrons and holes injected from cathode and anode produces light 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 the high efficiencies of device [14,15]. To overcome the imbalance of charge carrier injection or mobility, the most frequently used solutions have been either to use additional organic charge-transporting layers between the emissive layer and the electrodes or to adjust the energy band of the polymer by introduction of electron-withdrawing groups attached to the polymer backbone. It was shown by Bredas and Heeger that introduction of electron-withdrawing groups onto the arylene rings or the vinylene groups of the polymer, lowers the HOMO and LUMO energies of the polymer, thereby permitting the use of a higher work function metal in the LED device [16].

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PPVs are greenish-yellow light-emitting polymers [17,18]. However, to be utilized in the single-layer devices with higher work function metal as the cathode, PPV has the drawback that it is a poor electron acceptor due to its high LUMO energy. To improve the electron injection ability of the polymers, abundant derivatives of PPV have been reported with electron-withdrawing substituents such as halide [19−21], cyano [22,23], trifluoromethyl [24], or methylsulfonyl-phenyl [25] on the arylene rings. Other examples with electron-withdrawing groups on vinylene group of conjugated polymers have also been reported [8,26−29].

In our previous work [29], we reported the synthesis and electroluminescence properties of new EL polymers, poly(*p*-phenylenedifluorovinylene) (PPDFV) and poly(2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (DMOS−PPDFV), which contain two fluoro groups in every vinylene unit to reduce the barrier of electron injection. Here we report the synthesis of the copolymers with poly(2-ethylhexyloxy-5-methoxy-1,4-phenylenevinylene) (MEH−PPV) and DMOS−PPDFV by Gilch reaction [30,31]. Also, we synthesized the copolymers with poly(2-dimethyloctylsilyl-*p*-phenylenevinylene) (DMOS−PPV) and DMOS−PPDFV. Synthesized MEH-PPV-*co*-DMOS-PPDFVs and DMOS-PPV-*co*-DMOS-PPDFVs were incorporated with PPDFV, having two fluoro groups in every vinylene unit, to investigate the effect of the electron-withdrawing fluorine atom on the optical and device properties of the copolymers.

2. Experimental section

2.1. 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 Varian Gemini-200 (200 MHz), Unityplus-300 (300 MHz) and Inova-500 (500 MHz) spectrometers 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 system. For PL spectral 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. Isopropyl solution of the PEDOT/PSS was spin-coated onto 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 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 the 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 an EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s.

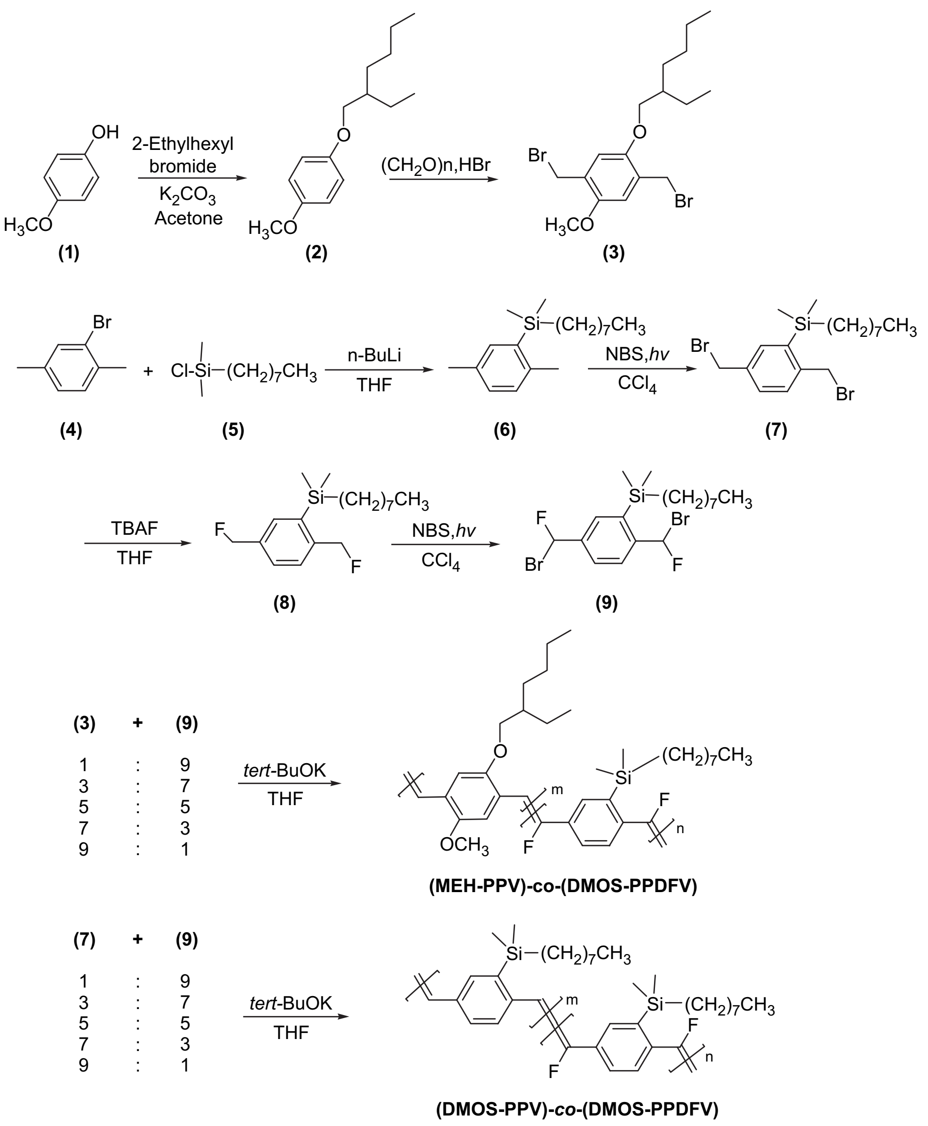
2.2. Polymer synthesis

MEH-PPV-*co*-DMOS-PPDFV and DMOS-PPV-*co*-DMOS-PPDFV with various feed ratios of MEH−PPV, DMOS−PPV and DMOS−PPDFV contents were synthesized. To a stirred solution of monomers **3** and **9**, or **7** and **9** (total amount of 0.85 mmol) in 20 mL of THF at 40 °C under argon was added 20.4 mL (5.10 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 color change from colorless to yellow green or orange yellow, and the viscosity was 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 powder. The resulting polymer was redissolved in 100 mL of THF (60 °C), cooled to 40 °C, and reprecipitated by drop-wise addition to 500 mL of methanol. The precipitated polymer was dried at room temperature under reduced pressure. This procedure was repeated once more using 1.0 L of THF/1.0 L of methanol to generate MEH-PPV-*co*-DMOS-PPDFVs and DMOS-PPV-*co*-DMOS-PPDFVs as orange yellow to yellow green powder.

3. Results and discussion

3.1. Synthesis and characterization

The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. In the first step, 4-methoxy phenol (**1**) was coupled with ethylhexyl bromide using potassium carbonate in acetone to generate 1-(2-ethylhexyloxy)-4-methoxybenzene (**2**), which was bromomethylated with paraformaldehyde and hydrobromic acid in acetic acid to provide 2,5-bis-(bromomethyl)-1-(2-ethylhexyloxy)-4-methoxybenzene (**3**). For the synthesis of another monomer unit **7**,



Scheme 1. Synthetic routes for monomers and polymers.

2-bromo-*p*-xylene (**4**) was coupled with chlorodimethyloctylsilane (**5**) using *n*-butyllithium in THF to generate dimethyloctylsilyl-*p*-xylene (**6**). This *p*-xylene was brominated using NBS and light source (300 W) to provide 2-dimethyloctylsilyl-1,4-bis(bromomethyl)benzene (**7**). The resulting dibromide **7** was fluorinated with tetrabutylammonium fluoride (TBAF) to generate compound **8**, which was brominated again using NBS and light source to generate 1,4-bis(bromofluoromethyl)-2-dimethyloctylsilylbenzene (**9**). The structure and purity of the monomers were confirmed by ^{1}H and ^{13}C NMR. Various feed ratios of monomers **3** and **9** were used for the preparation of MEH-PPV-*co*-DMOS-PPDFVs by the Gilch reaction, with an excess amount of potassium *tert*-butoxide in THF at 40 °C for 24 h under Ar atmosphere. In addition to this, monomers **7** and **9** were used for the preparation of DMOS-PPV-*co*-DMOS-PPDFVs. The copolymers were soluble in various organic solvents such as chloroform, chlorobenzene, THF, dichloromethane and ODCB. Table 1 summarizes the polymerization results and molecular weights of the copolymers.

The composition ratios of the MEH-PPV-*co*-DMOS-PPDFVs were measured by ^{1}H NMR. The composition ratios of MEH-PPV-*co*-DMOS-PPDFVs were determined by the proton peaks of the alkoxy groups of MEH–PPV and silyl group of DMOS–PPDFV. The deviation between the feed ratios and composition ratios can be caused by the different reactivity in the Gilch reaction with or without the fluoro groups on the monomers. In the case of DMOS-PPV-*co*-DMOS-PPDFV, it was not possible to detect the composition ratios since both monomer units have same silyl substituents on the arylene rings.

The results of molecular weights are also shown in Table 1. These copolymers have weight-average molecular weight (M_w) of 114,000–435,000 with polydispersity indices (M_w/M_n) of 1.44–2.68. The thermal properties of the copolymers

Table 1
Characterization of the PPDFV copolymers

PPDFV copolymers	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Feed ratio	MEH-PPV-*co*-DMOS-PPDFV					DMOS-PPV-*co*-DMOS-PPDFV				
	9:1	7:3	5:5	3:7	1:9	9:1	7:3	5:5	3:7	1:9
Yield (%)	65	62	48	52	42	53	53	52	49	45
M_w[a] ($\times 10^3$)	42.3	23.0	13.8	11.6	11.8	43.5	39.2	29.8	12.5	11.4
PDI[a]	2.46	1.96	1.77	1.50	1.44	2.68	2.56	2.19	1.60	1.62
T_d[b] (°C)	360	365	340	280	300	435	400	380	350	330
Composition ratio[c]	91.0/9.0	75.3/24.7	63.3/36.7	48.4/51.6	14.5/85.5					

[a] Molecular weight (M_w) and polydispersity index (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.

[c] Calculated from the results of NMR.

were determined by TGA measurements. All these copolymers show good thermal stability, with onset decomposition temperature (T_d, 5% weight loss) of 280–435 °C under nitrogen.

3.2. Absorption properties of the copolymers

The optical and photoluminescence properties of the copolymers were investigated both in THF solutions and in thin solid films. The concentration of all the THF solutions of the copolymers was fixed at 1×10^{-5} M. Transparent and uniform copolymer films were prepared on quartz plates by spin-casting from their respective *o*-dichlorobenzene (ODCB) solution at room temperature. The absorption and emission data for the copolymers are summarized in Table 3. MEH-PPV-*co*-DMOS-PPDFVs are expected to be useful for the tuning of the emission colors by the adjustment of the ratios of MEH–PPV unit having 2,5-dialkoxy groups which influence the effective conjugation length. With increased ratio of DMOS–PPDFV, the effective conjugation length is shortened as compared to the case of the copolymer with large ratio of MEH–PPV. As shown in Fig. 1, there is not much difference between the absorption spectra of the solutions and the thin films of the MEH-PPV-*co*-DMOS-PPDFVs, which can be attributed to the π–π* transitions of the copolymers. The MEH-PPV-*co*-DMOS-PPDFVs exhibit absorption spectra with maximum peaks at 372–497 nm. The maximum absorption peak at 372 nm was red shifted with more amount of the MEH–PPV. This is originated from the increase of the electron density along the π-conjugated polymer backbone by incorporation of the MEH–PPV segment and extension of the effective conjugation length of the copolymers. The absorption onset wavelengths of MEH-PPV-*co*-DMOS-PPDFVs were 506–593 nm, which correspond to band gaps of 2.09–2.45 eV.

In the case of DMOS-PPV-*co*-DMOS-PPDFVs, the maximum absorption peaks were at 377–427 nm, also attributed to π–π* transition of the conjugated backbones as shown in Fig. 2. Especially, the thin films of DMOS-PPV-*co*-DMOS-PPDFVs with ratios of 5:5, 3:7, 1:9 showed red shifted maximum absorption peaks as compared to the case of the solution. This was caused by the higher amounts of the difluoro-substituted vinylene units. But in the case of MEH-PPV-*co*-DMOS-PPDFVs, the red-shifting effect of the alkyloxy groups of the MEH–PPV units was dominating as compared to that of the difluoro-substituted vinylene units. Difluoro groups on the vinylic position of DMOS–PPDFV homopolymer induced the blue shift of the absorption spectrum as compared to the case of DMOS–PPV homopolymer, which was caused by the decrease of the effective conjugation length [29]. The absorption onset wavelengths of DMOS-PPV-*co*-DMOS-PPDFVs were

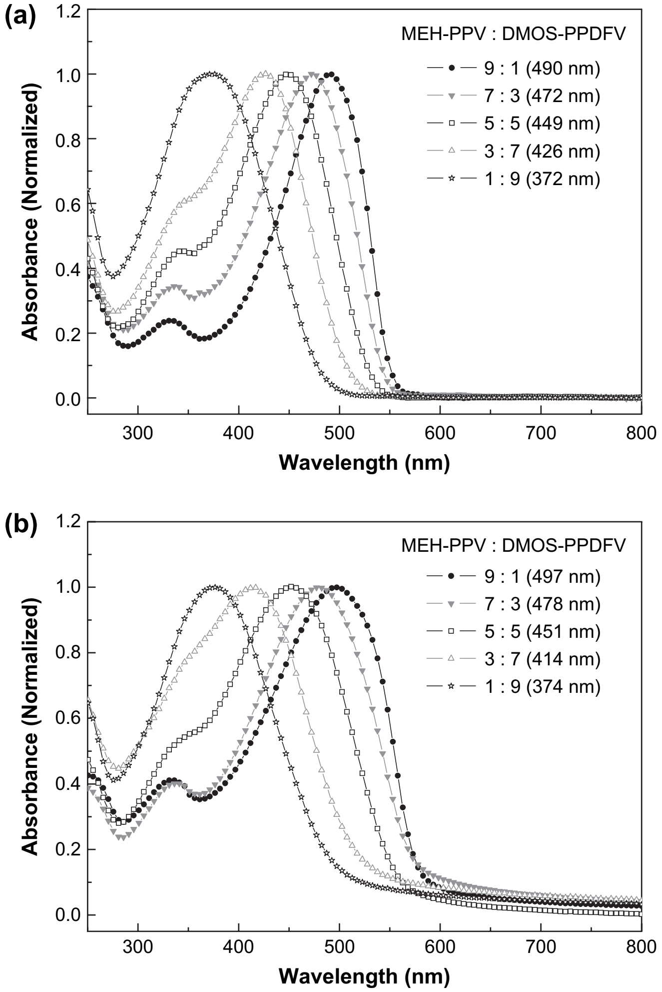


Fig. 1. UV–vis absorption spectra of the MEH-PPV-*co*-DMOS-PPDFVs (a) in the THF solution and (b) in thin film.

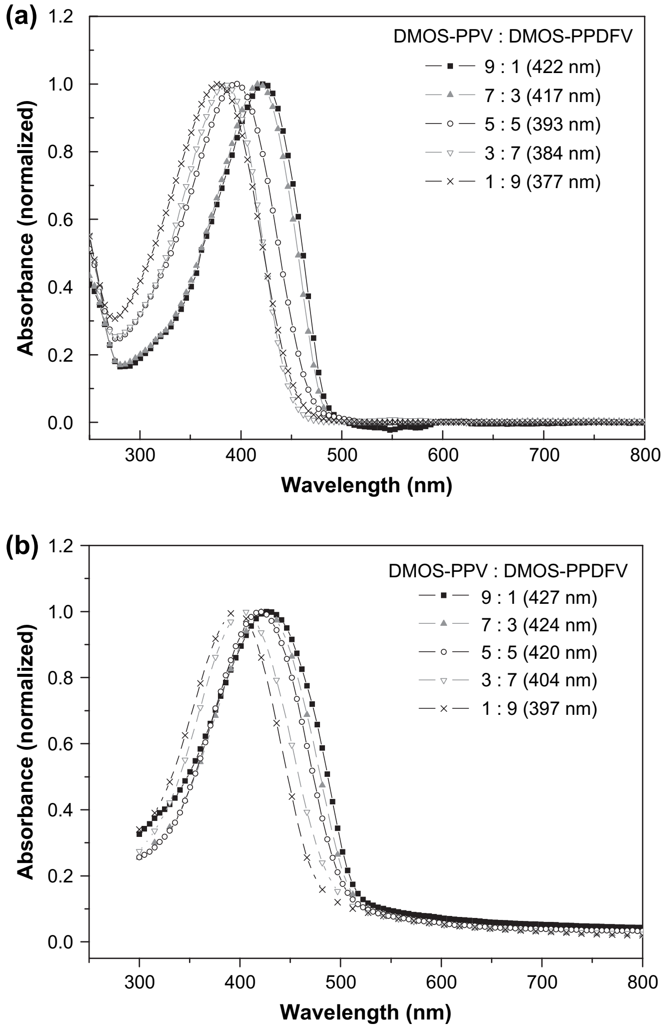


Fig. 2. UV–vis absorption spectra of DMOS-PPV-*co*-DMOS-PPDFVs (a) in the THF solution and (b) in thin film.

482–527 nm, which correspond to band gaps of 2.35–2.57 eV.

In the case of the UV spectra of MEH-PPV-*co*-DMOS-PPDFVs, a side peak at around 340 nm was noticed but DMOS-PPV-*co*-DMOS-PPDFV showed single peak. In the case of MEH-PPV-*co*-DMOS-PPDFVs, since the absorption spectrum of MEH–PPV is much different as compared to that of DMOS–PPDFV, the absorption peak of the fragment of DMOS–PPDFV was found at around 340 nm with lower ratios of DMOS–PPDFV. With more amount of DMOS–PPDFV, this side peak was shifted to around 370 nm which is the maximum peak of the copolymer with 1:9 ratio. In the case of DMOS-PPV-*co*-DMOS-PPDFV, since the absorption spectra of the two homopolymers are similar, the copolymer showed single peak.

3.3. Electrochemical properties of the polymers

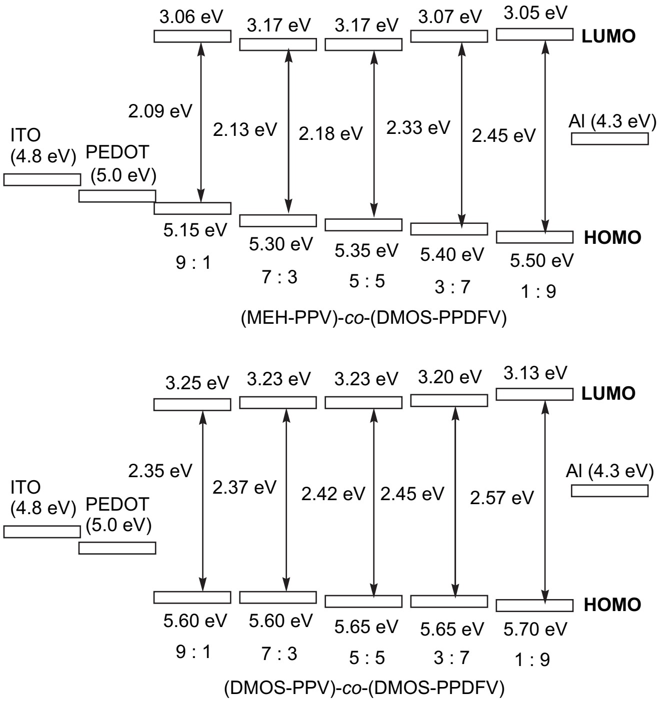


Fig. 3. Energy band diagram of the copolymers.

The energy band diagrams, as shown in Fig. 3, 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. The CV was performed with 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 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 2. HOMO levels were calculated according to the empirical formula ($E_{\mathrm{HOMO}} = -([E_{\mathrm{onset}}]^{\mathrm{ox}} + 4.65)$ (eV). During the anodic scan, the oxidation onset potentials of MEH-PPV-*co*-DMOS-PPDFVs and DMOS-PPV-*co*-DMOS-PPDFVs are in the range of

Table 2
Electrochemical potentials and energy levels of the PPDFV copolymers

PPDFV copolymers	E_{onset}[a] (V)	HOMO[b] (eV)	LUMO[c] (eV)	E_g[d] (eV)
1	0.50	−5.15	−3.06	2.09
2	0.65	−5.30	−3.17	2.13
3	0.70	−5.35	−3.17	2.18
4	0.75	−5.40	−3.07	2.33
5	0.85	−5.50	−3.05	2.45
6	0.95	−5.60	−3.25	2.35
7	0.95	−5.60	−3.23	2.37
8	1.00	−5.65	−3.23	2.42
9	1.00	−5.65	−3.20	2.45
10	1.05	−5.70	−3.13	2.57

[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.

0.48–0.85 and 0.95–1.05 V, and exhibited irreversible p-doping process. Fig. 3 shows the hypothesized energy diagrams of the ITO/PEDOT/polymer/Al device fabricated in this work. HOMO energy levels of the present EL copolymers are about 5.15–5.70 eV. The HOMO energy level of MEH–PPV and DMOS–PPV is 4.93 and 5.04 eV. When the DMOS–PPDFV contents in both of the copolymers were increased, the HOMO energy levels were decreased, which is caused by the electron-withdrawing effect of the fluoro group. In the case of MEH-PPV-*co*-DMOS-PPDFVs, with higher contents of DMOS–PPDFV, the band gap was increasing. This could be explained as the effect of the electron donating alkyloxy groups of MEH–PPV. With less amount of MEH–PPV, the backbone will have reduced electron density, which will cause the increase of the band gap.

In the case of DMOS-PPV-*co*-DMOS-PPDFVs, both of the monomers contain dimethyloctylsilyl (DMOS) group. With higher ratio of DMOS–PPDFV in the copolymers, there will be more amount of fluoro group on the vinylene units. With increased quantity of the electron-withdrawing fluoro groups on the vinylene, the backbone will have reduced electron density, which will cause the increase of the band gap. The LUMO energy level was calculated from the values of the band gap and HOMO energy level. In the case of the homopolymers, DMOS–PPDFV and DMOS–PPV, the LUMO levels were about same but the band gap of DMOS–PPDFV was increased about 0.5 eV as compared to that of DMOS–PPV, causing the HOMO level of DMOS–PPDFV to be decreased about 0.4 eV as compared to that of DMOS–PPV [29] The current copolymers showed same trend to show similar LUMO levels and increased band gaps with higher amount of DMOS–PPDFV. The electro-optical characteristics of the present polymers are summarized in Table 2.

3.4. PL properties of the polymers

Figs. 4 and 5 show the photoluminescence (PL) spectra of the copolymers in THF solutions and in thin film.

The PL spectrum of the MEH-PPV-*co*-DMOS-PPDFVs in solution exhibits emission maxima at around 513–544 nm, and vibronic features were not found. The PL spectrum of the MEH–PPV thin film exhibits a maximum at 590 nm, and that of the DMOS–PPDFV thin film exhibits a maximum at 495 nm. As the DMOS–PPDFV content increases in the

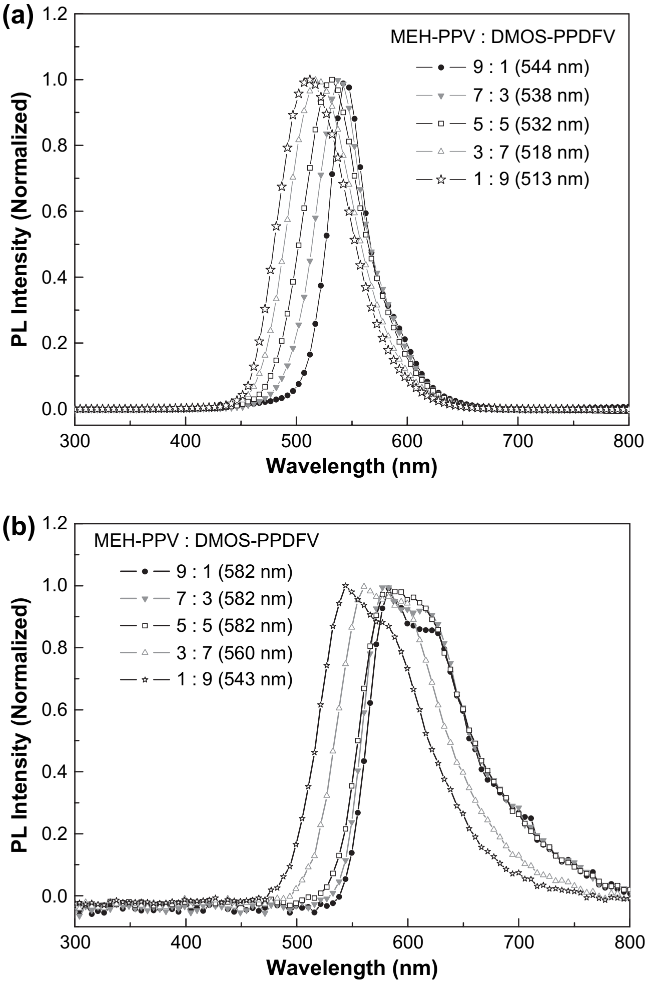


Fig. 4. Photoluminescence spectra of MEH-PPV-*co*-DMOS-PPDFVs (a) in the THF solution and (b) in thin film.

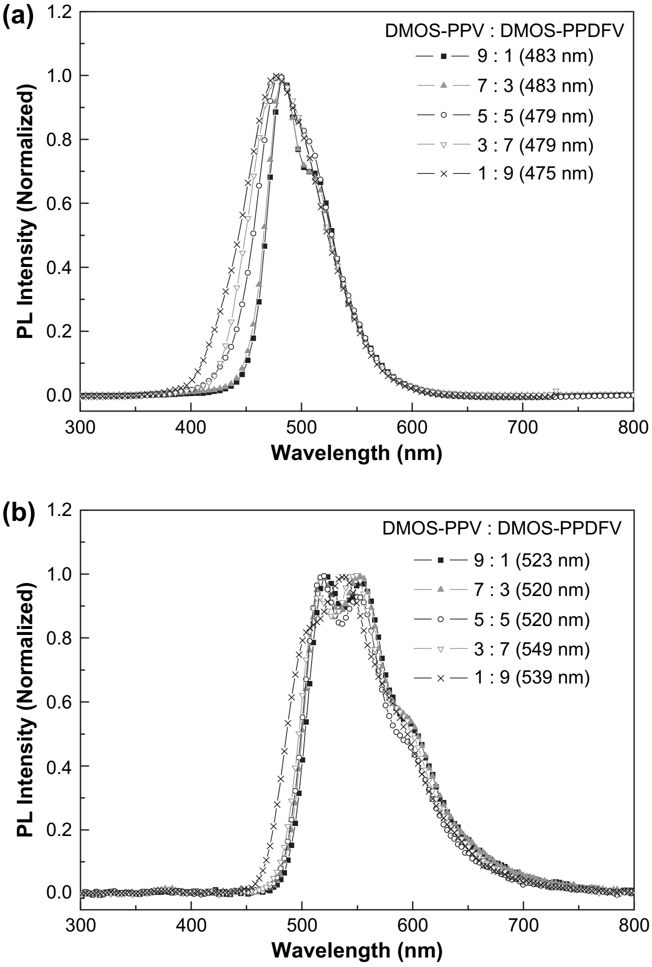


Fig. 5. Photoluminescence spectra of DMOS-PPV-*co*-DMOS-PPDFVs (a) in the THF solution and (b) in thin film.

Table 3
Optical properties of the PPDFV copolymers

PPDFV copolymers	Solution (nm)			Film λ_{max} (nm)		
	Abs λ_{max}	PL λ_{max}[a]	fwhm[b]	Abs λ_{max}	PL λ_{max}[a]	fwhm[b]
1	490	544	40	497	582 (621)	93
2	472	538	52	478	582 (616)	100
3	449	532	62	451	588 (605)	106
4	426	518	69	414	560 (593)	104
5	372	513	73	374	543 (582)	101
6	422	483 (510)	60	427	523 (552, 595)	101
7	417	483 (510)	61	424	520 (552, 595)	104
8	393	479 (510)	71	420	520 (549, 595)	86
9	384	479	76	404	549 (516, 595)	103
10	377	475	80	397	539 (510, 595)	109

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

copolymer system, the emission peaks of MEH-PPV-*co*-DMOS-PPDFVs thin film are blue-shifted from 582 to 543 nm. Such a blue shift for the copolymer system could be attributed to the decrease of the effective conjugation length of the copolymers. The subpeaks at 621–582 nm are caused by the aggregation of the copolymers. The full width at half-maximum (fwhm) was increased by 30–50 nm in the case of PLs of the thin films as compared to the case of solution. This can be attributed to the increased aggregation of the copolymers in thin film status possibly caused by the electron-withdrawing fluoro groups on the vinylene unit.

The PL spectrum of the DMOS-PPV-*co*-DMOS-PPDFVs in solution exhibits vibronic features at 510 nm and emission maxima at around 475–483 nm. The PL spectra of the copolymer films show emission maxima at the 523–539 nm region. The emission maximum at around 475–483 nm, observed in THF solutions, was not discernible in the copolymer films, suggesting the presence of aggregation of the copolymer main chains in the solid state. And, as the DMOS–PPDFV contents increase in DMOS-PPV-*co*-DMOS-PPDFVs, the band gap of the copolymers is increasing as shown Fig. 3. But the peak at around 539 nm, caused by the aggregation of the copolymers, is increasing with higher contents of DMOS–PPDFV. The fwhm was increased by 30–40 nm in the case of PLs of the thin films as compared to the case of solution of DMOS-PPV-*co*-DMOS-PPDFVs. This can also be attributed to the increased aggregation of the copolymers in thin film status possibly caused by the electron-withdrawing fluoro groups on the vinylene unit (Table 3).

3.5. Electroluminescent properties and current density–voltage–luminescence (J–V–L) characteristics

The current density–voltage and luminescence–voltage characteristics of ITO/PEDOT/polymer/Al devices are shown in Table 4. The turn-on voltages of ITO/PEDOT/polymer/Al devices are about 5–9 V. The luminescence intensities of polymers are exponentially increased with an increase in voltage. The maximum luminescence (L_{max}) of DMOS-PPV-*co*-DMOS-PPDFV (1:9) is 760 cd/m^2 at 7.5 V.

Fig. 6 shows the EL spectra of ITO/PEDOT/polymer/Al devices. The EL spectra of copolymers are similar to their PL spectra. This result indicates that the EL and PL phenomena originated from the same excited state. As compared to the PL spectra of thin films, the EL spectra of the copolymers showed decrease in the subpeak as shown in Fig. 6. The maximum EL peaks of MEH-PPV-*co*-DMOS-PPDFV are red shifted by 5–17 nm as compared to the PL spectra. DMOS-PPV-*co*-DMOS-PPDFVs (9:1, 7:3, 5:5, 3:7) showed the maximum EL peaks at about 514–516 nm. But in the case of DMOS-PPV-*co*-DMOS-PPDFV with 1:9 ratio showed the maximum EL peak at 543 nm caused by the aggregation. As was the case of PL spectra in solid state, this aggregation was caused by the higher ratio of the electron-withdrawing difluoro groups in the vinylene unit.

The emission colors of MEH–PPV and DMOS–PPDFV with the CIE coordinates of $x = 0.53$, $y = 0.46$ and $x = 0.40$, $y = 0.57$ are orange yellow and green. By adjusting the feed ratios of DMOS–PPDFV in MEH-PPV-*co*-DMOS-PPDFV, it was possible to tune the emission colors from orange yellow to yellow green depending on the obtained CIE coordinates. By increasing the feed ratio of DMOS–PPDFV, the CIE coordinates were moving from orange yellow to green. But in the case of DMOS-PPV-*co*-DMOS-PPDFV, the CIE coordinates were almost same.

As shown in Table 4, the luminescence efficiencies of the copolymers at room temperature were about 0.02–1.31 lm/W.

Table 4
Device performance characteristics of the PPDFV copolymers

PPDFV copolymers	EL λ_{max} (nm)	Turn-on voltage (V)	Voltage[a] (V)	Current density[a] (mA/cm^2)	Luminance[a] (cd/m^2)	LE$_{max}$[b] (lm/W)	CIE (x,y)[c]
1	577	7	8	74	41	0.055	0.53,0.46
2	571	8.5	13	377	261	0.067	0.53,0.46
3	571	6	7	99	59	0.059	0.51,0.48
4	554	7	10	452	74	0.016	0.43,0.54
5	538	6.5	11	207	275	0.132	0.40,0.57
6	514 (549)	9	18	48	133	0.048	0.34,0.60
7	514 (549)	5	7	26	76	0.13	0.32,0.60
8	514 (546)	5.5	6.5	19	240	0.60	0.33,0.60
9	516 (546)	5.5	8.5	1160	258	0.0083	0.33,0.60
10	543 (513)	5	7	26	698	1.31	0.35,0.56

[a] Measured under the condition of maximum luminescence efficiency.
[b] Maximum luminescence efficiency.
[c] Calculated from the EL spectrum.

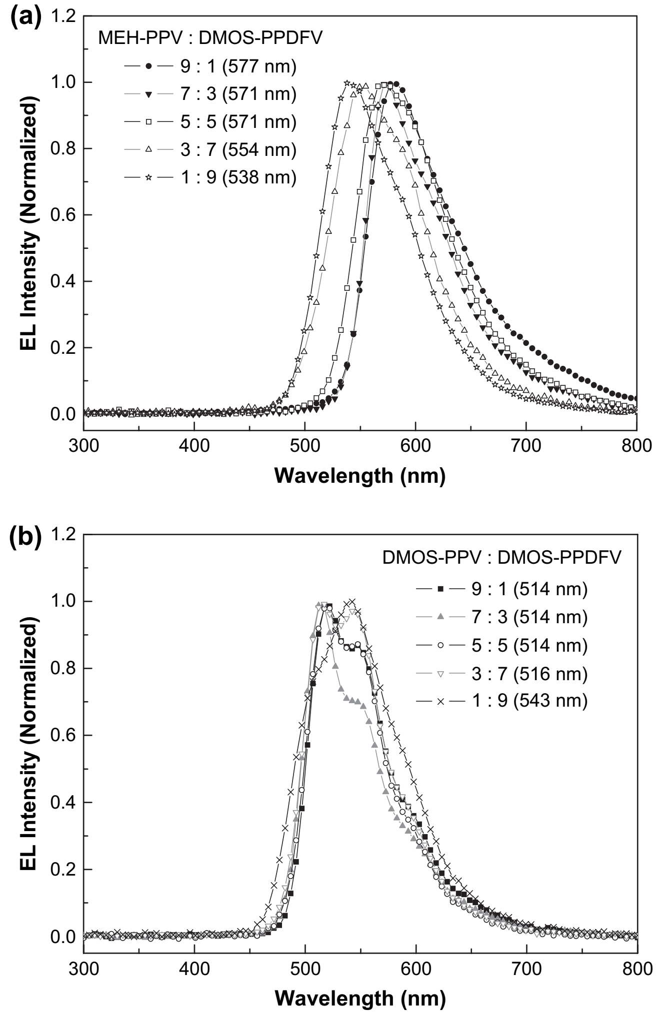


Fig. 6. Electroluminescence spectra of devices with the configuration of ITO/PEDOT/copolymers/Al.

In the case of DMOS-PPV-*co*-DMOS-PPDFV with 1:9 feed ratio showed the highest luminescence efficiency of 1.31 lm/W. It was reported before by us that the homopolymer DMOS–PPDFV with the difluoro groups on the vinylene unit showed higher efficiency as compared to the case of DMOS–PPV without the difluoro groups [29]. Both types of copolymers, MEH-PPV-*co*-DMOS-PPDFV and DMOS-PPV-*co*-DMOS-PPDFV, showed highest luminescence efficiencies, with the highest ratio of DMOS–PPDFV.

In general, as compared to the PL spectra in solution state, PL spectra in solid state and EL spectra of both types of copolymers showed red shifted and broader peaks caused by the aggregation. The broadening of the peaks by the introduction of the fluoro groups in the vinylene unit could be utilized in the generation of white color LEDs.

4. Conclusion

Copolymers with difluoro groups in vinylene unit, MEH-PPV-*co*-DMOS-PPDFV and DMOS-PPV-*co*-DMOS-PPDFV, were synthesized by the Gilch reaction. In both types of the copolymers, the band gaps were increasing with higher ratio of DMOS–PPDFV. The HOMO energy levels of both types of copolymers were about 5.15–5.70 eV, which is lower than the case of MEH–PPV and DMOS–PPV. The LUMO energy levels were about 3.06–3.25 eV, which is also lower than the case of MEH–PPV and DMOS–PPV.

As compared to the PL spectra in solution state, PL spectra in solid state and EL spectra of both types of copolymers showed red shifted and broad peaks caused by the aggregation. These effects are caused by the introduction of the fluoro groups in the vinylene unit.

The polymer LEDs of MEH-PPV-*co*-DMOS-PPDFVs emit light with maximum peaks at around from 538 to 577 nm. By adjusting the feed ratios of DMOS–PPDFV in the copolymers, we could tune the emission colors from orange yellow to green. DMOS-PPV-*co*-DMOS-PPDFVs (9:1, 7:3, 5:5, 3:7) showed the maximum EL peaks at about 514–516 nm. But in the case of DMOS-PPV-*co*-DMOS-PPDFV with 1:9 ratio showed the maximum EL peak at 543 nm caused by the aggregation. This aggregation was caused by the higher ratio of the electron-withdrawing difluoro groups in the vinylene unit.

The luminescence efficiencies of the copolymers at room temperature were about 0.02–1.31 lm/W. DMOS-PPV-*co*-DMOS-PPDFV with 1:9 feed ratio showed the highest luminescence efficiency of 1.31 lm/W.

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