Electroluminescence of Polymer Blend Composed of Conjugated and Nonconjugated Polymers. White-Light-Emitting Diode

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ABSTRACT: We report on the investigations of electroluminescence (EL) for the polymer blend composed of two organic soluble polymers. The blends consist of main chain conjugated poly[(2-methoxy-5-((2-ethylhexyl)oxy)-1,4-phenylene)vinylene] (MEH−PPV) and a side chain luminescent polymer, an alkoxy(trifluoromethyl)stilbene-substituted PMA derivative (CF_3−PMA). Emitting colors of the polymer blends varied with the blending ratios of two polymers. The electroluminescent peak of the MEH−PPV-rich polymer blend ranged over 580−800 nm (orange-red light), and of the CF_3−PMA-rich polymer blend ranged from 380 to 800 nm, resulting in a white-light emission. Additional new EL peaks of polymer blends at around 380 and 800 nm would originate from the CF_3−PMA and the exciplex formed by photoinduced electron transfer between two polymers.

Introduction

The potential for making a large area multicolor display from easily processible polymers has driven much of the recent research in the area of polymer light-emitting diodes (LEDs). A variety of materials have been investigated as active electroluminescent materials,[1−5] and a number of device structures have been proposed because it is important to find an appropriate device structure to maximize the carrier recombination efficiency.[6−10] Many kinds of conducting polymers and fluorescent dyes have been developed in order to obtain highly efficient electroluminescence (EL), long lifetime, white color emission,[11−14] and color variability[15−18] for the realization of display applications. The EL efficiency could be greatly enhanced by blending a polyconjugated polymer and a conjugation length regulated polymer or hole and electron transporting molecules.[19−21] In particular, it is important to obtain the white-light-emitting diode and color variability because this can permit a multicolor display and facilitate the fabrication process of multicolor displays. We have therefore focused on developing white-light-emitting EL devices, and Granstrom et al. have recently developed one made with polymer blends.[22]

In this paper, in order to obtain a white color LED, we have investigated novel polymer blends as the emitting layer; the blend is composed of a polyconjugated main chain polymer, poly[(2-methoxy-5-((2-ethylhexyl)oxy)-1,4-phenylene)vinylene] (MEH−PPV) and a nonconjugated side chain polymer, an alkoxy(trifluoromethyl)stilbene-substituted PMA derivative (CF_3−PMA). We discuss the results of optical measurements, luminescent behaviors and electrical characteristics of the device. Synthetic routes for CF_3−PMA and the polymer structure of MEH−PPV are shown in Scheme 1.

Experimental Section

Instrumentation. Synthesized compounds were identified by ^1H- and ^{13}C-NMR spectra which were obtained using a Bruker AM 200 spectrometer. FT-IR spectra were measured by using a Bomem Michelson series instrument. UV−visible spectra of the MEH−PPV, CF_3−PMA, and polymer blends were measured using a Shimadzu UV-3100s. Photoluminescence (PL) spectra of the polymer blends were obtained using a Perkin-Elmer LS-50 luminescence spectrometer. Electroluminescence (EL) spectra were measured using a monochromator (ISA HR-320) with the photomultiplier tube (Hammamatsu R955) as a detector. EL spectra were recorded at 3 nm resolution through the photon counter (SR400) averaging the signal from PMT while applying direct current from the current/voltage source (Keithley 238). For the characterization of device properties, current−electric field strength (I−F) characteristics was measured using a current/voltage source and an optical powermeter (Newport 835). The injected current was measured by the voltage supply while applying forward bias. All the measurements mentioned above were performed in air and at room temperature.

Poly[(2-methoxy-5-((2-ethylhexyl)oxy)-1,4-phenylene)vinylene], (MEH−PPV). MEH−PPV was synthesized by the method reported by Wudl et al.[23] The final polymer was soluble in common organic solvents.

Alkoxy(trifluoromethyl)stilbene-Substituted PMA Derivative, (CF_3−PMA). CF_3−PMA was synthesized by the following procedures.

Diethyl 4-(Trifluoromethyl)benzylphosphonate (1). Compound **1** was prepared by reacting 15 g (63 mmol) of 1-(bromomethyl)-4-(trifluoromethyl)benzene with 12 mL (69 mmol, 1.1 equiv) of triethyl phosphite at 80 °C for 7 h and then removed the unreacted triethyl phosphite under reduced pressure. The product was a colorless liquid, and the yield was 17 g (90%): bp 110 °C/25 Torr. ^1H-NMR ($CDCl_3$, ppm): δ 7.42 (m, 4H), 3.99 (m, 4H), 3.15 (d, 2H), 1.20 (t, 6H). ^{13}C-NMR($CDCl_3$, ppm): δ 135.69, 129.80, 124.97, 121.12, 115.72, 61.84, 34.64, 31.89, 15.85. FT-IR (KBr pellet, cm^{-1}): 3050 (aromatic C−H), 2960 (aliphatic C−H), 1620 (aromatic C=C), 1250 (P=O), 1170 (aromatic C−F).

4-((6-Hydroxyhexyl)oxy)benzaldehyde (2). A solution of 20 g (164 mmol) of 4-hydroxybenzaldehyde, 27 g (186 mmol, 1.1 equiv) of K_2CO_3, and 26 mL (186 mmol, 1.1 equiv) of 1-chloro-6-hydroxyhexane in 100 mL of DMF was stirred and

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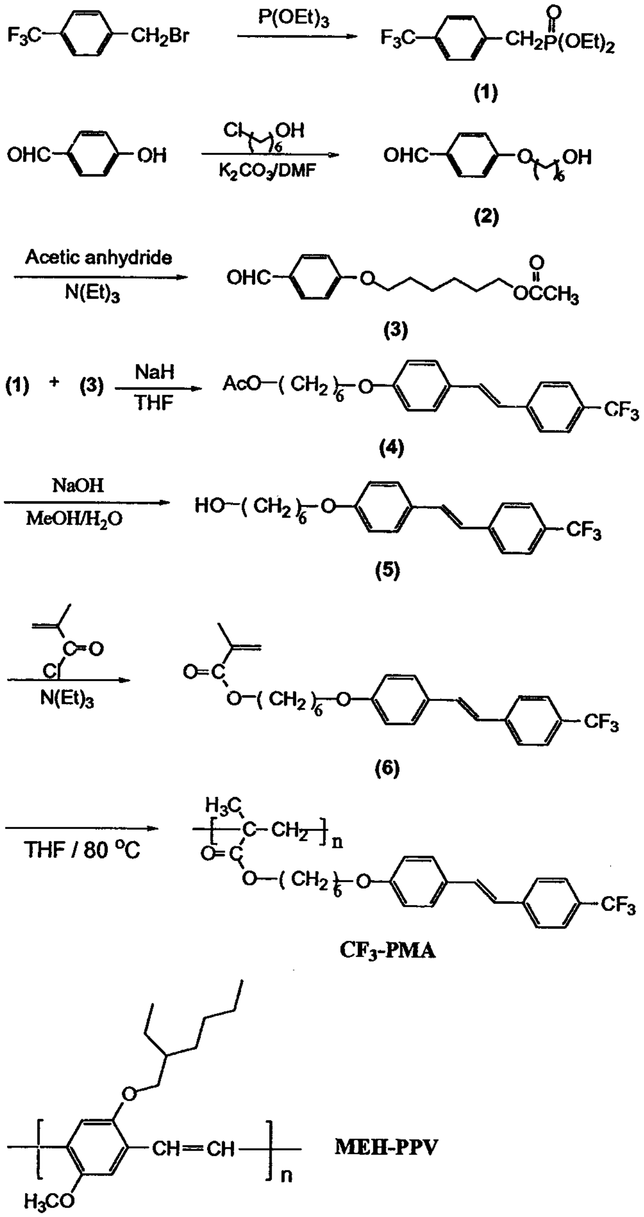
Scheme 1



heated to 80 °C for 24 h. The resulting mixture was poured into water and then extracted with ethyl acetate and water solution. The organic layer was collected and dried with anhydrous MgSO4. After filtration and concentration, the product was obtained as a white powder by recrystallization with *n*-hexane. The product yield was 20 g (55%): mp 44.8−46.7 °C. ^{1}H-NMR (CDCl$_3$, ppm): δ 9.77 (s, 1H), 7.72 (d, 2H), 6.90 (d, 2H), 3.95 (t, 2H), 3.57 (t, 2H), 2.46 (s, 1H), 1.78−1.30 (m, 8H). ^{13}C-NMR(CDCl$_3$, ppm): δ 190.78, 164.08, 131.84, 129.51, 114.59, 68.11, 62.41, 32.38, 28.82, 25.61, 25.35. FT-IR (KBr pellet, cm^{-1}): 3450 (OH), 3050 (aromatic C−H), 2910 (aliphatic C−H), 1670 (aromatic C=O), 1605 (aromatic C=C).

6-(4-Formylphenoxy)hexyl Acetate (3). To synthesize compound **3**, 13 g (58 mmol) of compound **2**, 9 mL (87 mmol, 1.5 equiv) of acetic anhydride, and 8.9 mL (87 mmol, 1.5 equiv) of triethylamine were stirred in methylene chloride at room temperature for 5 h. The reaction mixture was extracted with methylene chloride and NaOH solution. The organic layer was concentrated and then purified with column chromatography. The product was a solid, giving 12 g (78%): mp 33.8−35.4 °C. ^{1}H-NMR (CDCl$_3$, ppm): δ 9.77 (s, 1H), 7.87 (d, 2H), 7.70 (d, 2H), 3.95 (m, 4H), 1.94 (s, 3H), 1.73−1.30 (m, 8H). ^{13}C-NMR-(CDCl$_3$, ppm): δ 190.47, 170.86, 163.94, 131.72, 129.59, 114.52, 67.96, 64.11, 28.70, 28.29, 25.44, 25.39, 20.72. FT-IR (KBr pellet, cm^{-1}): 3060 (aromatic C−H), 2910 (aliphatic, C−H), 1740 (aliphatic C=O), 1690 (aromatic C=O),1605 (aromatic C=C).

6-[4-{2-(4-(Trifluormethyl)phenyl)vinyl}phenoxy]hexyl Acetate (4). First, 10 g (34 mmol) of phosphonate **1** and 9 g (34 mmol) of aldehyde **3** were dissolved in 100 mL of THF and added to 1.2 g (51 mmol, 1.3 equiv) of NaH carefully, and then the mixture was refluxed for 10 h. The reaction mixture was poured into the water to give a crude powder. The crude product was purified by the recrystallization in methanol. The product yield was 10 g (81%): mp 124.4−125.9 °C. ^{1}H-NMR (CDCl$_3$, ppm): δ 7.54 (s, 4H), 7.43 (d, 2H), 7.12 (d, 1H), 6.94 (d, 1H), 6.88 (d, 2H), 4.06 (t, 2H), 3.96 (t, 2H), 2.04 (s, 3H), 1.80−1.43 (m, 8H) (s, 18H). ^{13}C-NMR(CDCl$_3$, ppm): δ 171.1, 159.27, 141.13, 130.71, 129.20, 127.99, 126.19, 125.52, 125.44, 124.76, 118.33, 115.70, 67.79, 64.37, 22.06, 28.48, 25.67, 25.62, 20.90. FT-IR (KBr pellet, cm^{-1}): 3030 (aromatic C−H), 2920 (aliphatic C−H), 1740 (aliphatic C=O), 1607 (aromatic C=C), 1130 (aromatic C−F).

6-[4-{2-(4-(Trifluormethyl)phenyl)vinyl}phenoxy]hexan-1-ol (5). Compound **5** was prepared by reacting 6.5 g (16 mmol) of compound **4** with an excess of NaOH in methanol/water cosolvent at 80 °C for 3 h. When the reaction was finished, the reaction mixture was poured into cold water to give a crude white product. Further purification was performed by recrystallization in methanol. The product yield was 5.3 g (90%) ; mp 161.8−162.9 °C. ^{1}H-NMR (CDCl$_3$, ppm): δ 7.54 (s, 4H), 7.44 (d, 2H), 7.12 (d, 1H), 6.94 (d, 1H), 6.88 (d, 2H), 3.97 (t, 2H), 3.65 (t, 2H), 1.79−1.42 (m, 8H), 1.53 (s, 1H). ^{13}C-NMR (CDCl$_3$, ppm): δ 159.31, 141.17, 130. 74, 129.21, 128.01, 126.21, 125.56, 125.48, 124.79, 118.33, 115.74, 67.90, 62.81, 31.61, 29.17, 25.84, 25.51. FT-IR (KBr pellet, cm^{-1}) 3300 (OH), 3020 (aromatic C−H), 2920 (aliphatic C−H), 1605 (aromatic C=C), 1130 (aromatic C−F).

6-[4-{2-(4-(Trifluormethyl)phenyl)vinyl}phenoxy]hexyl 2-Methylacrylate (6). Monomer **6** was prepared by reacting 5 g (13.7 mmol) of compound **5** and 1.9 mL of methacryloyl chloride (16.4 mmol, 1.2 equiv) in 2 mL of triethylamine and 30 mL of methylene chloride at room temperature for 4 h. The resulting mixture was washed several times with water and then dried with anhydrous MgSO4. After filtration and concentration, the product was obtained as a white powder by recrystallization with methanol. The product yield was 5 g (85%): mp 113.8−114.9 °C. ^{1}H-NMR (CDCl$_3$, ppm): δ 7.55 (s, 4H), 7.43 (d, 2H), 7.11 (d, 1H), 6.94 (d, 1H), 6.88 (d, 2H), 6.09 (m, 1H), 5.54 (m, 1H), 4.15 (t, 2H), 3.97 (t, 2H), 1.92 (s, 3H), 1.80−1.46 (m, 8H). ^{13}C-NMR-(CDCl$_3$, ppm): δ 167.46, 159.29, 141.14, 136.47, 130.73, 129.20, 128.00, 126.20, 125.46, 125.38, 125.15, 124.76, 118.34, 115.72, 67.81, 64.57, 29.08, 28.51, 25.75, 25.69, 18.26. FT-IR (KBr pellet, cm^{-1}): 3020 (aromatic C−H), 2900 (aliphatic C−H), 1710 (C=C-C=O), 1605 (aromatic C=C), 1125 (aromatic C−F).

CF$_3$−PMA. A solution of 1 g (2.3 mmol) of monomer **6** in 5 mL of anhydrous THF was prepared, and then 5 mg of benzoyl peroxide (BPO) was added as a catalyst and reacted at 70 °C for 2 days under N$_2$ atmosphere. After 2 days, the reaction mixture was added dropwisely into the large amount of methanol. The crude polymer, CF$_3$−PMA, was precipitated, filtered, and then purified by using a Soxhlet extractor for 5 days in methanol. The polymer yield was 0.95 g (95%). FT-IR (KBr pellet, cm^{-1}): 3020 (aromatic C−H), 2920 (aliphatic C−H), 1725 (aliphatic C=O), 1610 (aromatic C=C), 1170 (aromatic C−F). T_m = 169 °C.

Polymer Blend. The structually different polymers MEH−PPV and CF$_3$−PMA were blended by changing the weight ratios of the two polymers in organic solvents. Thin films of the polymer blends could be obtained by spin-cast from the solution with excellent reproducibility, and they were very homogeneous and showed no phase separation or aggregation between two polymers. The LED structures consist of an aluminum rectifying contact on the polymer blend which was coated on the ITO electrode acting as a hole-injecting contact. The film thickness ranged from 80 nm to 100 nm. Electron-injecting aluminum contacts were formed by vacuum evaporation at pressure below 10^{-6} Torr, giving active areas of 0.2 cm^2.

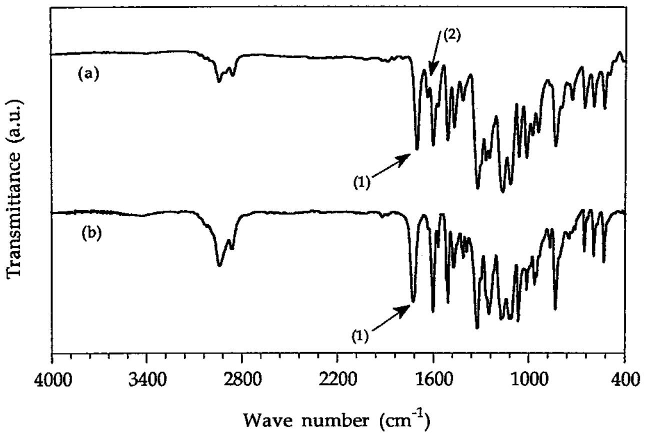


Figure 1. FT-IR spectra of (a) acrylate monomer and (b) CF_3−PMA.

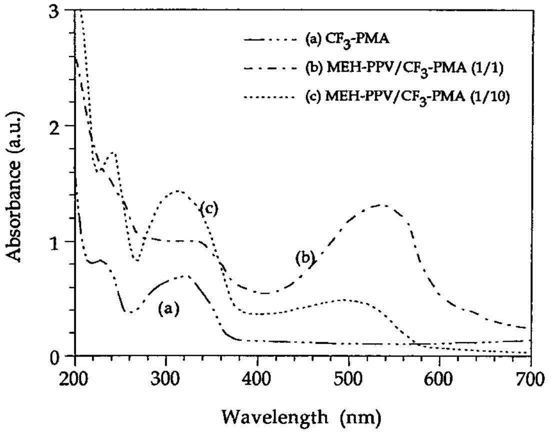


Figure 2. UV−visible spectra of CF_3−PMA and polymer blends.

Results and Discussion

Figure 1 shows FT-IR spectra of the acrylate monomer and CF_3−PMA polymer. In Figure 1a, the acrylate monomer shows a strong absorption peak for the conjugated carbonyl group (1) at 1710 cm^{-1} and also the characteristic stretching C=C absorption peak (2) of the acrylate group at 1610 cm^{-1}. After radical polymerization, peak 1 was shifted to 1725 cm^{-1} (Figure 1b), corresponding to the aliphatic C=O stretching mode, and peak 2 also disappeared because of the polymerization through the double bond of the acrylate monomer. The molecular weight of CF_3−PMA(M_n = 36 000, M_w = 158 000, PDI = 4.4) is reasonably high for film-casting, and the polymer is easily soluble in common organic solvents such as cyclohexanone and tetrahydrofuran.

UV−visible absorption spectra of CF_3−PMA and its polymer blends with MEH−PPV are shown in Figure 2. The maximum absorption and absorption edge of CF_3−PMA are shown at around 320 and 380 nm, respectively. Absorption peaks of the polymer blends were located at about 320 and 540 nm, corresponding to the component polymers, but absorbances were changed depending on the blending ratios. There are no new absorption bands in the spectra of the polymer blends, and it may indicate that there is no interaction between MEH−PPV and CF_3−PMA in the ground state.

To measure the emission properties of the polymers, they were excited at 320 nm under air and room temperature condition. PL spectra of the polymers are shown in Figure 3. The PL spectrum of CF_3−PMA has a peak at 420 nm, indicating blue light emission.

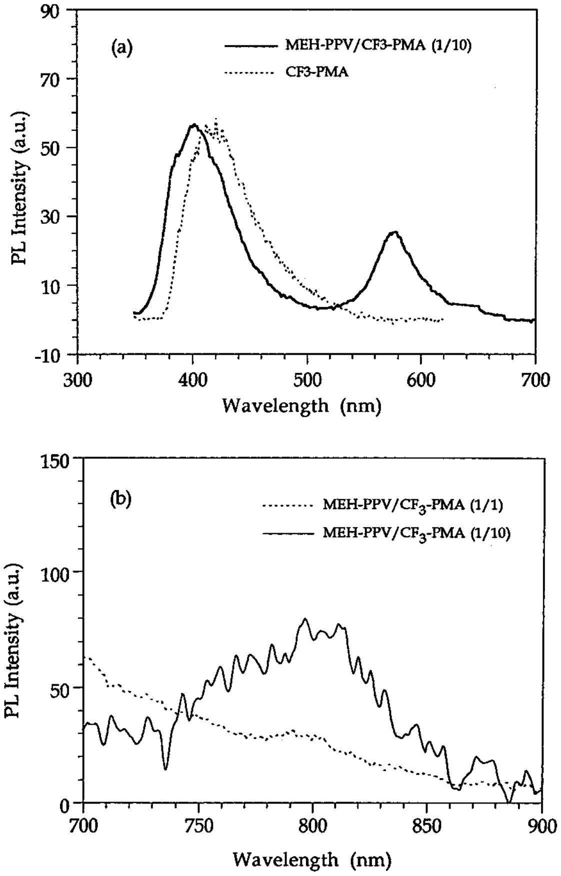


Figure 3. PL spectra of (a) CF_3−PMA and MEH/CF_3−PMA (1/10) polymer blend and (b) the same spectra extended over a longer wavelength region (excited at 320 nm).

However, the PL spectrum of the MEH−PPV/CF_3−PMA (1/10) blended polymer showed two isolated emission peaks at 400 and 580 nm corresponding to the component polymers, indicating both blue and yellow light emissions, respectively. Figure 3b shows the PL spectra extended over a long wavelength region of the polymer blend thin films excited at 320 nm. Interestingly, new and long wavelength emissions were observed at around 800 nm. The MEH−PPV/CF_3−PMA (1/1) polymer blend showed very weak emission, but in the case of the MEH−PPV/CF_3−PMA (1/10) polymer blend, a highly intense red light emission at around 800 nm was observed. It is well-known that the electronically excited states are more easily reduced or oxidized than the corresponding ground states.[24] We expect that the excited CF_3−PMA would be a good acceptor of electrons donated from MEH−PPV in its ground state, leading to the formation of an exciplex from the photoinduced electron transfer. Similarly, the CF_3−PMA/MEH−PPV exciplex can also be formed by the interaction of excited MEH−PPV with the ground state CF_3−PMA. In these results, the PL emission profiles of the polymer blends consist of three components; blue emission originating from CF_3−PMA (420 nm), yellow emission from MEH−PPV (580 nm), and the exciplex emission from both polymers (800 nm), indicating that a white light emission can be obtained.

EL spectra of the polymer blends also exhibit three components emissions (shown in Figure 4), similar to the PL spectra. The additional long wavelength emission of EL spectra may also result from the exciplex emission between two polymers. It is hard to obtain directly the EL emission from the CF_3−PMA homopolymer because of the difficulty of carrier injection and

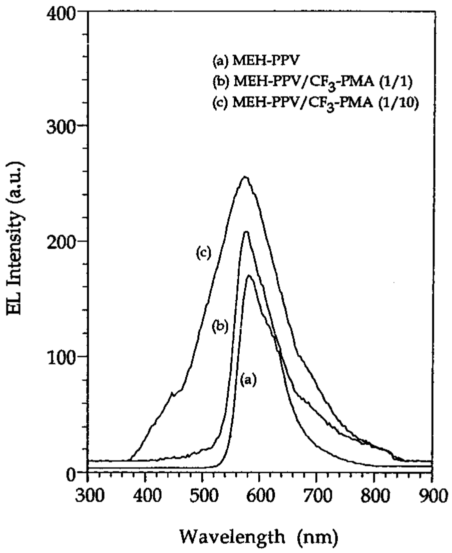


Figure 4. EL spectra of MEH−PPV and its CF$_3$−PMA polymer blends.

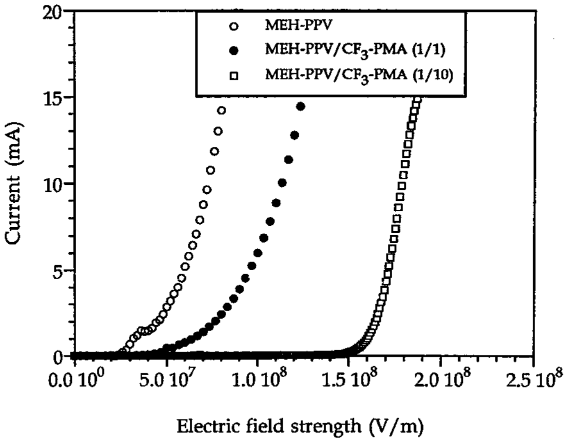


Figure 5. Current−electric field strength (I−F) characteristics of MEH−PPV and CF$_3$−PMA polymer blends.

mobility. Generally, a forward current is affected by a carrier injection and mobility in matrix. The forward current of ITO/CF$_3$−PMA/Al system was not obtained under a high forward bias, which indicates that the energy barrier between the ITO and the HOMO state of CF$_3$−PMA is very high, and the carrier mobility in the CF$_3$−PMA is very low. But, in the blended systems, the current as well as the EL emission was obtained under a forward bias. Therefore, we guess that MEH−PPV, which has the low energy barrier for the hole injection, assists the carrier transportation through the polymer matrix. And, it seems that MEH−PPV acts as a carrier transporting polymer as well as an EL emitting polymer, so that the portion of CF$_3$−PMA may radiate blue light, to give a white light emitting LED. The emission color of MEH−PPV/CF$_3$−PMA (1/10) device was nearly white, but unfortunately time stability of the device was not satisfactory. Though we did not measured the lifetime of the device, the devices showed a lower life time than that of any other polyconjugated polymer, especially PPV, so additional efforts are being performed to obtain a long-term stable LED.

Figure 5 shows the current−electric field strength (I−F) characteristics measured from MEH−PPV and its CF$_3$−PMA blends. The forward bias current was obtained when the ITO is a positive electrode and Al electrode is grounded. The forward current increases with increasing forward bias voltage for all devices. The turn-on voltages of the polymer blend devices increased as the contents of the nonconjugated CF$_3$−PMA increased, and operating electrical field strengths of polymer blends were on the order of 10^8 V/m.

Conclusion

A new alkoxy(trifluoromethyl)stilbene-substituted PMA derivative was prepared and blended with MEH−PPV. PL and EL properties of the polymer blends were investigated. The emissions from MEH−PPV/CF$_3$−PMA (1/10) blended LED consist of peaks of 400, 580, and 800 nm corresponding to blue, yellow, and red light, respectively, to give a white light. The additional long wavelength emssions in PL and EL for the polymer blend may be caused by the red-shifted exciplex formed by two polymers. Conclusively, we could obtain a white-light-emitting diode by blending conjugated MEH−PPV and nonconjugated CF$_3$−PMA.

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