

Synthesis of Copolyfluorenes with High Fluorenone Contents and Its Application in Electroluminescent Device by Simple Blending

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ABSTRACT: Poly(fluorene-co-fluorenone)s containing high contents of fluorenone chromophore were synthesized by the Suzuki coupling reaction to study their electroluminescent (EL) properties. The copolymers are thermally stable below 430°C (T_d) in nitrogen atmosphere. In film state, their absorption and photoluminescence spectra (peaked at 373–382 nm and 562–564 nm, respectively) are mainly originated from fluorenone units, because of its efficient energy transfer. Both LUMO and HOMO energy levels, estimated from their cyclic voltammograms, are lowered slightly ($-3.17 \rightarrow -3.23$ eV, $-5.84 \rightarrow -5.89$ eV) with increasing contents of electron-withdrawing fluorenone units. Double-layer EL devices,

using the copolyfluorenes or their blends with poly(9,9-dihexylfluorene) (PF) as emitting layer, show exclusive emission originated from fluorenone chromophore (565 nm) when its content is high. Blending 0.02–5 wt % of PF-33 (fluorenone fraction: 0.37) with PF greatly enhances device performance ($610 \text{ cd m}^{-2} \rightarrow 4400 \text{ cd m}^{-2}$ and $0.45 \text{ cd A}^{-1} \rightarrow 1.52 \text{ cd A}^{-1}$). Our results demonstrate that the copolyfluorenes are promising emitting materials for EL devices by simple blending. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2576–2583, 2011

Key words: electroluminescent; copolyfluorene; fluorenone; copolymer

INTRODUCTION

Considerable interests have been attracted to develop light-emitting diodes (LEDs) based on conjugated polymers, because of their wide-range applications.^{1–3} Most studies were focused on exploring efficient and thermally stable light-emitting polymers.^{4,5} Polyfluorene and its derivatives are considered as the most potential candidate for efficient and stable blue-emitting materials.⁶ However, imbalance of charge-carriers' injection and mobility in polyfluorene-based light-emitting devices was still a challenge for high efficient PLEDs. This imbalance is mainly caused by the difference between injection barrier height and/or mobility for holes and those for electrons. As most of the conjugated polymers are favorable for hole injection, accordingly the imbalance can be prevented by using conjugated polymers having lowest unoccupied molecular level (LUMO level) as emitting layer.^{7,8}

Polyfluorene reveals blue-fluorescence with the emission wavelength located at 400–460 nm,^{3,9,10} and

its fluorescence quantum yields are 60–80% in solution or solid state. Moreover, polyfluorene is thermally and chemically stable, because of its unique chemical structure. These characteristics make polyfluorene suitable for fabricating blue-emitting electroluminescent (EL) devices.^{11,12} However, undesirable green emission at about 500–550 nm appears under device operation or thermal annealing that causes the emission color to shift from blue to blue-greenish. The low-energy emission was first regarded to be caused by molecular chain aggregation.¹³ Subsequently, Miller and coworkers proposed, it was attributed to intermolecular excimer induced by oxidation at C-9 of fluorene units.^{14,15} List suggested that the low-energy emission was because of keto effect, that is, forming fluorenone moiety by electro-and-photo-oxidative degradation of polyfluorene devices.¹⁶ Hintschich and coworkers studied the intramolecular fluorescence quenching in luminescent copolymers containing fluorenone and fluorene units.^{17–19} Jenekhe and coworkers incorporated different ratios (0–10 mol %) of fluorenone units into polyfluorene and found that the luminance increased with fluorenone contents (0 mol %, 280 cd m^{-2} ; 10 mol %, 2360 cd m^{-2}).²⁰ Pei's group also incorporated 0–25 mol % fluorenone and obtained similar results.²¹ White polymer light-emitting-diode was fabricated by Heeger's group via

Additional Supporting Information may be found in the online version of this article.

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blending poly(fluorene-co-fluorenone) with transition metal complex.²² Yang and coworkers used the fluorenone defect property of polyfluorenes to fabricate high luminescent white-light device with maximum luminance and luminance efficiency of 4800 cd m⁻² and 3 cd A⁻¹, respectively.²³ However, the compositions of fluorenone units were lower than 25 mole percents, and so far as we know no poly(fluorene-co-fluorenone) has been reported. Preparation and systematic study of copolyfluorenes containing high contents of fluorenone repeat unit would be interesting and useful for EL applications.

Herein, we present synthesis, characterization, and EL properties of copolyfluorenes containing high contents of fluorenone chromophore. The feed compositions of the electron-withdrawing fluorenone chromophore are 33–60 mol %. Their photoluminescence (PL) spectra in film state (excitation: 378 nm) are mainly originated from fluorenone chromophores (562–564 nm), because of efficient energy transfer. However, their electrochemical properties change slightly with increasing contents of fluorenone units. Blending of the copolyfluorene (**PF-33**) with **PF** significantly enhances the EL performance, indicating that the copolyfluorenes are useful for optoelectronic devices.

EXPERIMENTAL

Materials

All starting materials were purchased from Aldrich (Germany), TCI (Tokyo, Japan), or Acros (USA) and used without further purification. Solvents such as chloroform (CHCl₃, Tedia, USA), methanol (Tedia, USA), pyridine (Acros, USA), and toluene (Tedia, USA) were purified by the conventional method or used as received. The fluorenone contents in copolyfluorenes were controlled by varying the ratios of 2,7-dibromofluorenone (**M1**) in the feed (33–60 mol %). The copolyfluorenes were named as **PF-X** and **PF-Y**, in which **PF-Xs** and **PF-Ys** were consisting of fluorenone and 9,9-dihexylfluorene units (X and Y represent mole percents of **M1** in the feed).

Measurements

The FTIR spectra were measured (KBr pellet) using a Fourier transform infrared spectrometer, model 7850 from Jasco. The ¹H NMR spectra was obtained on a Bruker AVANCE-400 NMR spectrometer with chemical shifts reported in ppm using tetramethylsilane as an internal standard. The thermogravimetric analysis (TGA) of the copolymers was measured under nitrogen atmosphere at a heating rate of 20°C min⁻¹ using a Perkin-Elmer TGA-7 thermal analyzer. Absorption spectra were obtained with a Jasco V-550 spectrometer; PL spectra were recorded with a

Hitachi-4500 fluorescence spectrophotometer. The thin films used for spectroscopic measurements were obtained by casting polymer solutions (5 mg dL⁻¹) onto a quartz window and dried successively at ambient temperature, 50°C, and *in vacuo*. The cyclic voltammograms (CV) of the copolymers were measured at room temperature under nitrogen atmosphere using a copolymer-coated ITO glass as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum wire electrode as the auxiliary electrode. The electrodes were supported in dry acetonitrile containing 0.1M (*n*-Bu)₄NClO₄ as an electrolyte. The energy levels were calculated using the ferrocene (FOC) value of -4.8 eV with respect to vacuum level, which is defined as zero.^{24,25}

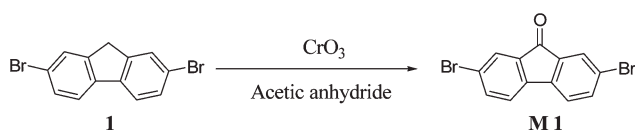
Double-layer EL devices [ITO/PEDOT:PSS/copolymer/Ca/Al] were fabricated by successive spin-coating of an aqueous solution of PEDOT and PSS (Baytron P from Bayer) as hole-injection layer and polymer (10 mg mL⁻¹ in toluene) as emissive layer onto transparent ITO glass. Finally, calcium and aluminum were deposited onto the polymeric film as cathode via vacuum deposition under 1.8 × 10⁻⁶ torr. The devices were fabricated in ambient conditions, and then their optoelectronic performance was measured in a glove box filled with nitrogen. Device performance and electroluminescence spectra were investigated and recorded, respectively, using a combination of Keithley power supply (model 2400) and Ocean Optics usb2000 fluorescence spectrophotometer.

Synthesis of 2,7-dibromo-9-fluorenone (**M1**)

A mixture of 2,7-bromofluorene (**1**: 1.94 g, 6 mmol), CrO₃ (1.50 g, 15 mmol) and acetic anhydride (45 mL) were stirred at 0°C for 1 h, followed by stirring at room temperature for 6 h.²⁶ The mixture was poured into a large amount of aqueous solution containing hydrochloric acid (2 wt %) (scheme 1). The appearing precipitate was collected by filtration and washed with cool water. The crude product was recrystallized from ether to give white solid of **M1** (yield: 88.6%, mp: 202–204°C). ¹H NMR (CDCl₃, ppm): δ 7.76 (s, 2H, Ar H), 7.61–7.63 (d, 2H, *J* = 8 Hz, Ar H), 7.37–7.39 (d, 2H, *J* = 8 Hz, Ar H). FTIR (KBr pellet, cm⁻¹): ν 1721 (C=O), 1605 (C=C), 1446. Anal. Calcd. (%) for C₁₃H₆Br₂O: C, 46.20; H, 1.79. Found: C, 46.19; H, 1.85.

Synthesis of **PF** and poly(fluorene-co-fluorenone)s

The polyfluorene and poly(fluorene-co-fluorenone)s were synthesized from 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (**2**), 2,7-dibromo-9,9-dihexylfluorene (**3**) and 2,7-dibromo-9-fluorenone (**M1**) via the palladium-catalyzed Suzuki coupling polycondensation (scheme 2). For example, a mixture of



Scheme 1 Synthesis of 2,7-dibromo-9-fluorenone (**M1**).

2 (0.5 g, 1 mmol), **3** (0.5 g, 1 mmol), 2M K_2CO_3 (4 mL), several drops of aliquat 336, and $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in 20 mL toluene was stirred at 90°C for 48 h. Phenylboronic acid (0.008 g, 0.067 mmol) and bromobenzene (0.01 g, 0.067 mmol) were subsequently added to the reaction mixture and reacted for 12 h after each addition. The mixture was poured into chloroform (100 mL) and washed thoroughly with aqueous solution of hydrochloric acid (2 wt %). The organic layer was collected and vacuum dried with a rotary evaporator. The residue was dissolved in chloroform and reprecipitated from methanol/ H_2O (v/v = 10/1) several times to obtain crude product. The crude product was then extracted with acetone for 24 h using a Soxhlet extractor. Reprecipitation of its solution in $CHCl_3$ from a large quantity of methanol gave rise to white-gray solid of **PF** (0.457 g, yield: 70.2%). FTIR (KBr pellet, cm^{-1}): ν 1456 ($-C=C-$), 2853, 2926, 2952 ($-CH_2-$). 1H NMR ($CDCl_3$, ppm): δ 7.83–7.85 (s, 2H, Ar-H), 7.67–7.71 (d, 4H, Ar-H), 2.12 (m, 4H, $-CH_2-$), 1.13 (m, 16H, $-CH_2-$), 0.75–0.81 (m, 6H, $-CH_3$). Anal. Calcd. (%) for $C_{25}H_{32}$: C, 90.30; H, 9.63. Found: C, 89.56; H, 9.76.

The synthetic procedures of copolymers **PF-40**–**PF-60** were analogous to those used in the preparation of **PF**, except that 2,7-dibromo-9-fluorenone (**M1**) was used instead of **3**, whereas **PF-33** and **PF-40** were prepared by direct copolymerization of dibromo monomers **M1** and **3** with diborate monomer **2**.

PF-40 (yield: 59%). FTIR (KBr pellet, cm^{-1}): ν 1456 ($-C=C-$), 1606 ($-C=C-$), 1720 ($-C=O-$), 2854, 2924, 2950 ($-CH_2-$). 1H NMR ($CDCl_3$, ppm): δ 8.05 (s, 2H, Ar-H), 7.81–7.84 (m, 6H, Ar-H), 7.64–7.74 (m, 4H, Ar-H), 2.09 (m, 4H, $-CH_2-$), 1.10–1.25 (m, 16H, $-CH_2-$), 0.76–0.78 (m, 6H, $-CH_3$). Anal. Calcd. (%) for $C_{25}H_{32}$: C, 88.89; H, 7.76. Found: C, 87.56; H, 7.51.

PF-48 (yield: 62%). FTIR (KBr pellet, cm^{-1}): ν 1456 ($-C=C-$), 1606 ($-C=C-$), 1721 ($-C=O-$), 2856, 2924, 2950 ($-CH_2-$). 1H NMR ($CDCl_3$, ppm): δ 8.05 (s, 2H, Ar-H), 7.81–7.87 (m, 6H, Ar-H), 7.57–7.75 (m, 4H, Ar-H), 2.09 (m, 4H, $-CH_2-$), 1.09–1.25 (m, 16H, $-CH_2-$), 0.75–0.79 (m, 6H, $-CH_3$). Anal. Calcd. (%) for $C_{25}H_{32}$: C, 89.10; H, 7.49. Found: C, 87.48; H, 7.63.

PF-50 (yield: 72%). FTIR (KBr pellet, cm^{-1}): ν 1454 ($-C=C-$), 1606 ($-C=C-$), 1720 ($-C=O-$), 2854, 2922, 2950 ($-CH_2-$). 1H NMR ($CDCl_3$, ppm): δ 8.00–8.06 (s, 2H, Ar-H), 7.82–7.87 (m, 6H, Ar-H), 7.61–

7.67 (m, 4H, Ar-H), 2.05–2.17 (m, 4H, $-CH_2-$), 1.09–1.25 (m, 16H, $-CH_2-$), 0.75–0.79 (m, 6H, $-CH_3$). Anal. Calcd. (%) for $C_{25}H_{32}$: C, 89.27; H, 7.73. Found: C, 86.21; H, 7.39.

PF-52 (yield: 85%). FTIR (KBr pellet, cm^{-1}): ν 1456 ($-C=C-$), 1606 ($-C=C-$), 1721 ($-C=O-$), 2860, 2918, 2950 ($-CH_2-$). 1H NMR ($CDCl_3$, ppm): δ 8.01–8.06 (s, 2H, Ar-H), 7.82–7.84 (m, 6H, Ar-H), 7.65–7.67 (m, 4H, Ar-H), 2.09 (m, 4H, $-CH_2-$), 1.09–1.25 (m, 16H, $-CH_2-$), 0.76–0.79 (m, 6H, $-CH_3$). Anal. Calcd. (%) for $C_{25}H_{32}$: C, 89.16; H, 7.52. Found: C, 87.19; H, 7.33.

PF-60 (yield: 71%). FTIR (KBr pellet, cm^{-1}): ν 1456 ($-C=C-$), 1606 ($-C=C-$), 1721 ($-C=O-$), 2855, 2924, 2950 ($-CH_2-$). 1H NMR ($CDCl_3$, ppm): δ 7.96–8.06 (m, 2H, Ar-H), 7.76–7.87 (m, 6H, Ar-H), 7.41–7.68 (m, 4H, Ar-H), 2.10 (m, 4H, $-CH_2-$), 1.10–1.25 (m, 16H, $-CH_2-$), 0.75–0.79 (m, 6H, $-CH_3$). Anal. Calcd. (%) for $C_{25}H_{32}$: C, 89.13; H, 7.20. Found: C, 86.84; H, 6.94.

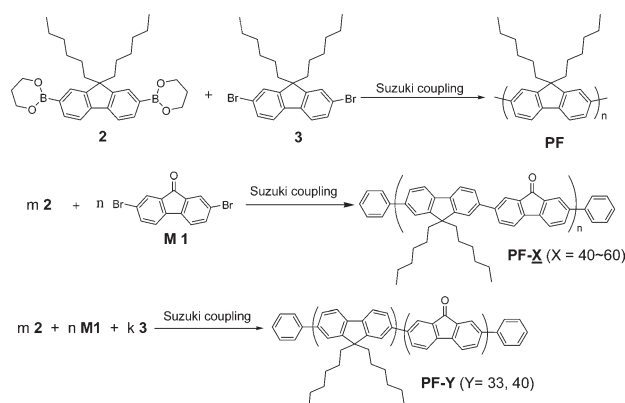
PF-33 (yield: 69%). FTIR (KBr pellet, cm^{-1}): ν 1456 ($-C=C-$), 1604 ($-C=C-$), 1720 ($-C=O-$), 2854, 2938, 2950 ($-CH_2-$). 1H NMR ($CDCl_3$, ppm): δ 8.06 (s, 2H, Ar-H), 7.75–7.87 (m, 6H, Ar-H), 7.47–7.69 (m, 4H, Ar-H), 2.11–2.17 (m, 4H, $-CH_2-$), 0.93–1.25 (m, 16H, $-CH_2-$), 0.76–0.79 (m, 6H, $-CH_3$). Anal. Calcd. (%) for $C_{25}H_{32}$: C, 89.60; H, 8.10. Found: C, 87.76; H, 8.15.

PF-40 (yield: 65%). FTIR (KBr pellet, cm^{-1}): ν 1456 ($-C=C-$), 1606 ($-C=C-$), 1722 ($-C=O-$), 2860, 2918, 2950 ($-CH_2-$). 1H NMR ($CDCl_3$, ppm): δ 8.01–8.06 (m, 2H, Ar-H), 7.73–7.87 (m, 6H, Ar-H), 7.56–7.68 (m, 4H, Ar-H), 2.09 (m, 4H, $-CH_2-$), 1.09–1.11 (m, 16H, $-CH_2-$), 0.75–0.79 (m, 6H, $-CH_3$). Anal. Calcd. (%) for $C_{25}H_{32}$: C, 88.89; H, 7.76. Found: C, 87.26; H, 7.61.

RESULTS AND DISCUSSION

Polymer preparation and characterization

Monomer **M1** (2,7-dibromo-9-fluorenone) was prepared by straight oxidation of 2,7-dibromofluorene



Scheme 2 Synthesis of copolyfluorenes **PF-X** and **PF-Y**; X and Y represent mole percents of 2,7-dibromo-9-fluorenone (**M1**) in the feed.

(1) with CrO_3 (Scheme 1). Copolyfluorenes **PF-X** and **PF-Y** were synthesized by the palladium-catalyzed Suzuki coupling polycondensation (Scheme 2). Distribution of 9,9-dihexylfluorene and fluorenone units in **PF-Xs** is alternate; because they were obtained by the direct coupling of 2,7-dibromo-9-fluorenone (**M1**) and 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (**2**). However, the distribution in **PF-Y** is a random one. The molecular weights of the **PF-Xs** were controlled by molar fractions of **M1** (0.4–0.6) in the feed. The **PF-Ys** were prepared from **2**, **3**, and **M1** (feed mole fractions of **M1**: 0.33, 0.4). The yields, molecular weights, and thermal properties of the resulted copolyfluorenes are summarized in Supporting Information Table S1. The weight-average molecular weights (M_w) of **PF-Xs** depend on molar fractions of **M1**, revealing a maximum value of 19 kg mole^{-1} at 0.52 (Supporting Information Fig. S1). The solubility of the copolyfluorenes depends mainly on their compositions, that is, they are readily soluble in chloroform and chlorobenzene when fluorenone fractions are lower than 0.5, such as **PF-33**, **PF-40**, **PF-40**, and **PF-48**. However, **PF-50** and **PF-60** are only partially soluble and **PF-52** is insoluble in the solvents, indicating that increased molecular weight leads to reduced solubility. Oldridge et al. synthesized soluble polyfluorenone by introducing bulky aromatic groups.²⁷ Compositions of the copolymers were determined from the ^1H NMR peak areas at 8.06 ppm (ortho proton at fluorenone unit) and 2.11 ppm (methylene proton at fluorene unit),^{20,21} and checked with elemental analysis data. For **F-33** and **PF-40**, the actual mole fractions of fluorenone in copolymers were 0.37 and 0.44, respectively, indicating that the reactivity of 2,7-dibromo-9-fluorenone (**M1**) is higher than 2,7-dibromo-9,9-dihexylfluorene (**3**), because of the presence of electron-withdrawing ketone groups. All copolymers show characteristic infrared absorptions of fluorenone unit at 1453, 1606, and 1720 cm^{-1} , among which the absorption at 1720 cm^{-1} is attributed to the stretching vibration of $\text{C}=\text{O}$ group in fluorenone unit. Thermal properties of the copolyfluorenes were investigated by thermogravimetric and differential scanning calorimetric measurements. The copolyfluorenes showed high thermal resistance and the weight losses at 430°C were lower than 5%. Moreover, the glass transition temperatures (T_g) of **PF-33**, **PF-40**, and **PF-52** were 87.6, 92.4, and 94.3°C, respectively, which increase slightly with increasing fluorenone contents.

Photophysical properties of poly(fluorene-co-fluorenone)s

The absorption spectra of **PF-33**, **PF-40**, and **PF-50** in chloroform are very similar in terms of feature and intensity, showing a main peak at 374–378 nm with

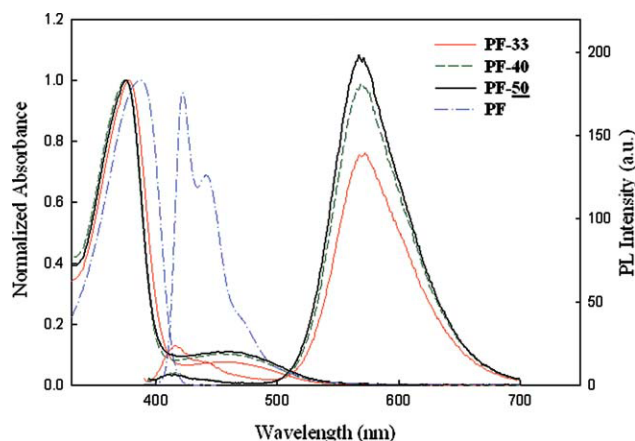


Figure 1 Absorption and PL spectra of **PF** and copolyfluorenes (**PF-33**, **PF-40**, **PF-50**) in CHCl_3 ; the concentration was 10^{-5}M and the excitation wavelength was 378 nm for PL spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a weak, broad shoulder at about 455–461 nm (Fig. 1, Table I). They are ascribed to the $\pi-\pi^*$ and $n-\pi^*$ transitions of fluorene and fluorenone moieties, respectively. Their PL spectra reveal strong emission of fluorenone units at 568 nm in addition to weak emission at 416 nm originated from $S_{10} \rightarrow S_{00}$ relaxation of the fluorene chromophore,²⁸ whose intensity is enhanced with an increase in fluorenone fractions. More importantly, the fluorenone emission (568 nm) is enhanced with an increase in fluorenone fractions, accompanied with simultaneous degeneration in fluorene emission (416 nm). This is attributable to efficient Förster energy transfer (from fluorene to fluorenone units) at high fluorenone fractions. However, the formation of an intramolecular charge transfer complex between fluorene segments and fluorenone units cannot be excluded.¹⁸ The PL spectra of **PF-33**, **PF-40**, and **PF-50** in film state also exhibit similar trend (Fig. 2), that is, enhanced emission at 562–564 nm and degenerated emission at 416 nm. The distance between polymer chains decreases dramatically as they change from solution to film state, which accordingly promotes the energy transfer that leads to significantly enhanced emission of the long wavelength chromophores.

As the carbonyl groups are readily protonated by protons, the emission behaviors of the copolyfluorenes should be strongly dependent on the concentration of protonic acid. Figure 3 shows the absorption and PL spectra of **PF-33** in CHCl_3 solution (10^{-5}M) containing various concentrations of acetic acid (1.67, 3.34, 6.67M). With increasing concentration in acetic acid, the absorption spectral feature exhibits little variation. However, the PL intensity at long wavelength region ($\sim 568 \text{ nm}$) decreases gradually, accompanied with slight blue-shift. In contrast, the PL intensity at about 416 nm exhibits steady increase

TABLE I
Optical Properties of the Copolyfluorenes

Copolymer	UV-vis λ_{\max} solution (nm)	UV-vis λ_{\max} film (nm)	PL λ_{\max} solution (nm)	PL λ_{\max} film (nm)
PF-40	369, 455	373, 450s ^a	416, 441, 566	563
PF-48	374, 459	379, 451s	416, 568	563
PF-50	375, 460	381, 450s	416, 568	562
PF-52	375, 461	-- ^b	416, 568	-- ^b
PF-60	372, 455	376, 451s	416, 568	562
PF-33	378, 457	382, 451s	416, 568	563
PF-40	374, 455	379, 451s	416, 568	564

^a The s means the absorption of shoulder.

^b Homogeneous PF-52 film could not be obtained because of its poor solubility.

simultaneously. As the carbonyl groups of fluorenone units are readily protonated by acetic acid,^{26,29} the lone pair electrons on oxygen are no longer easily movable. This will interrupt the excitation of fluorenone and/or energy transfer from fluorene to fluorenone; accordingly enhances the emission of fluorene unit (~ 416 nm) with simultaneous quenching of the long wavelength emission (~ 568 nm). This obvious acid-sensitive quenching and enhancing responses in PL emission is potentially applicable for pH-sensor, which is now under evaluation in our lab.

Electrochemical properties of poly(fluorene-co-fluorenone)s

Cyclic voltammetry (CV) was employed to study the reduction and oxidation behaviors of the copolyfluorenes films deposited on the working electrode (ITO). Onset reduction and onset oxidation potentials were used to estimate the LUMO and HOMO energy levels, respectively. The CV of PF-33, PF-40,

and PF-48 are shown in Supporting Information Figure S2 and their electrochemical data are summarized in Supporting Information Table S2. The onset reduction potentials ($E_{\text{onset}(\text{red})}$) of PF-33, PF-40, and PF-48 versus ferrocene ($E_{\text{FOC}} = 0.45$ V) are -1.63 V, -1.61 V, and -1.57 V, respectively, from which the LUMO energy levels are estimated to be -3.17 eV, -3.19 eV, and -3.23 eV. Their onset oxidation potentials ($E_{\text{onset}(\text{ox})}$) versus ferrocene are 1.04 V, 1.05 V, and 1.09 V, respectively. By similar methods, the HOMO energy levels of PF-33, PF-40, and PF-48 are estimated to be -5.84 eV, -5.85 eV, and -5.89 eV. Accordingly, the electrochemical band gaps (E_g^{el}) are 2.66 – 2.67 eV using the equation $E_g^{\text{el}} = \text{LUMO} - \text{HOMO}$. However, the optical band gaps estimated from edge absorption are 2.92 – 3.01 eV, which reveal large deviation (0.25 – 0.35 eV) from the electrochemical band gaps. This discrepancy in band gaps can be attributed to the difference in the estimation bases. Under an external potential, the electrons are injected mainly into fluorenone units because of its

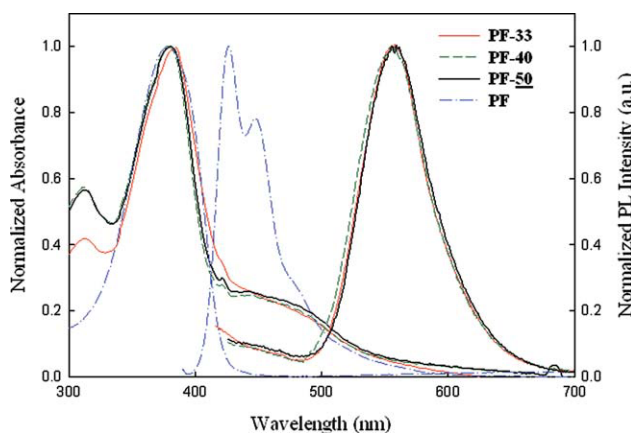


Figure 2 Absorption and PL spectra of PF and copolyfluorenes (PF-33, PF-40, PF-50) in film state; the excitation wavelength was 378 nm for PL spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

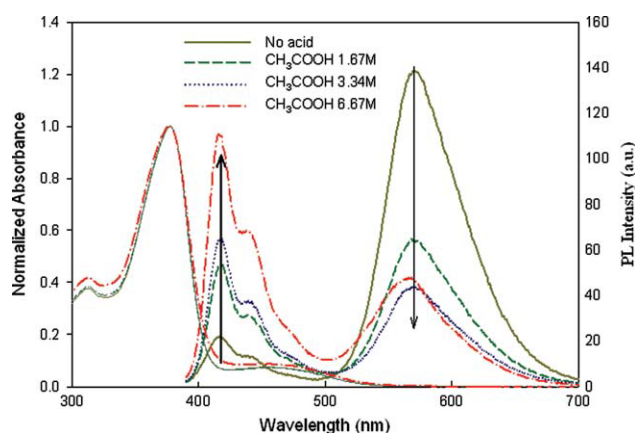


Figure 3 Effect of the concentration of acetic acid on absorption and PL spectra of PF-33 in CHCl_3 ; the concentration was 10^{-5} M and the excitation wavelength was 378 nm for PL spectra. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

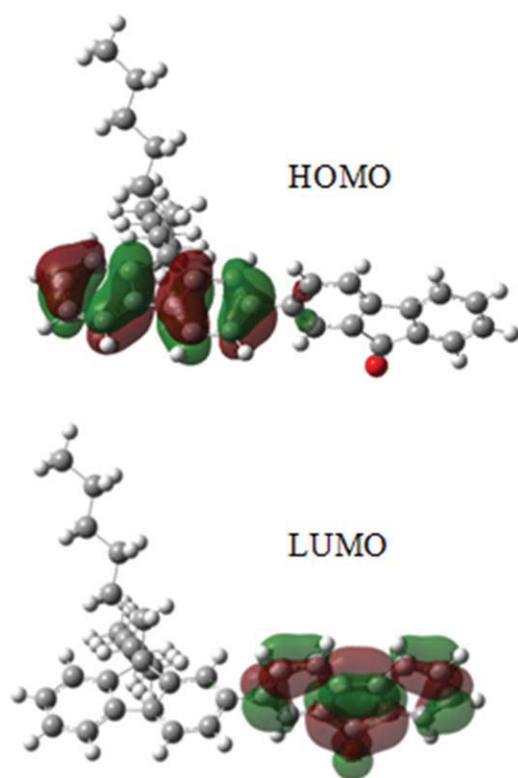


Figure 4 Optimized geometries and molecular orbital of linked fluorene and fluorenone, obtained from semi-empirical MNDO calculation (in gas phase). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electron-withdrawing characteristics. On the contrary, the holes are mostly injected into fluorene units. Therefore, the electrochemically-determined band gap (E_g^{el}) is actually the energy difference between LUMO of fluorenone units and HOMO of fluorene units. However, the optical band gap is estimated from edge absorption, which is actually the onset absorption of the chromophores having longer wavelength absorption (low-energy).

The HOMO levels of **PF-33** and **PF-40** (−5.84–−5.85 eV) are slightly higher than other copolymers (−5.87–−5.91 eV), implying that they possess better hole-injection ability. This is mainly attributed to their lower concentration of electron-withdrawing fluorenone units. However, electron affinity of the

copolymers is enhanced with increasing fluorenone contents, as shown in the LUMO levels of **PF-33**, **PF-40**, and **PF-48** (−3.17, −3.19, and −3.23 eV, respectively). Semi-empirical MNDO calculation was used to simulate the optimized geometries and molecular orbital of the copolyfluorenes represented by linked fluorenone–fluorene unit. The HOMO and LUMO are situated at the fluorene and fluorenone units (Fig. 4), respectively, which construct a coplanar main chain structure. Therefore, the holes and electrons prefer to inject into the fluorene and fluorenone units, respectively, which is coincident with the results obtained in electrochemical investigation.

Optoelectronic properties of EL devices

Double-layer EL devices, with a structure of (ITO/PEDOT:PSS/copolyfluorene/Ca/Al), were fabricated by successive spin-coating of hole-transporting PEDOT:PSS and emitting copolyfluorene layers, followed by vacuum deposition of metal cathode. The turn-on voltages (at a current density of 5 mA cm^{-2}) of **PF-33**, **PF-40**, and **PF-48** are 6.8 V, 6.2 V, and 5.2 V, respectively, decreasing with an increase in fluorenone fractions (Table II). However, the maximum luminance is decreased from 709 cd m^{-2} to 119 cd m^{-2} with increasing fluorenone fractions. This can be interpreted by longer life-time of fluorenone at excited state (S_1) (about 8–10 ns) that raises the ratio of radiationless decay of the excitons.²⁰ The EL emission (ca. 565 nm) of **PF-33**, **PF-40**, and **PF-48** are exclusively originated from fluorenone units (Fig. 5). At high fluorenone fractions the emission of fluorene units (400–450 nm) disappears completely, because of efficient energy transfer and/or predominant carriers recombination at fluorenone units.

We attempted to improve the device performance by blending with **PF**. For instance, the emitting layer was blends of **PF-33** (0.02, 0.5, 1, and 5 wt %) and **PF**. Supporting Information Figure S3 shows current density versus voltage and luminance versus voltage characteristics of double-layer devices using the blends or **PF** as emission layer. The turn-on voltages are between 9.2 V and 18 V (Table III), depending on the weight percents of **PF-33**. The turn-on voltage

TABLE II
Optoelectronic Properties of EL Devices Based on **PF-33**, **PF-40**, and **PF-48**^a

Emitting layer	Turn-on Voltage (V)	Maximum Luminance (cd m^{-2})	CIE Coordinates (x, y) ^a	FWHM ^b (nm)
PF-33	6.8	709	(0.45, 0.52)	93
PF-40	6.2	313	(0.45, 0.52)	108
PF-48	5.2	119	(0.45, 0.52)	97

^a Device configuration: ITO/PEDOT:PSS/Copolymer/Ca/Al. The CIE coordinates are calculated at maximum luminance.

^b FWHM: full width at half maximum.

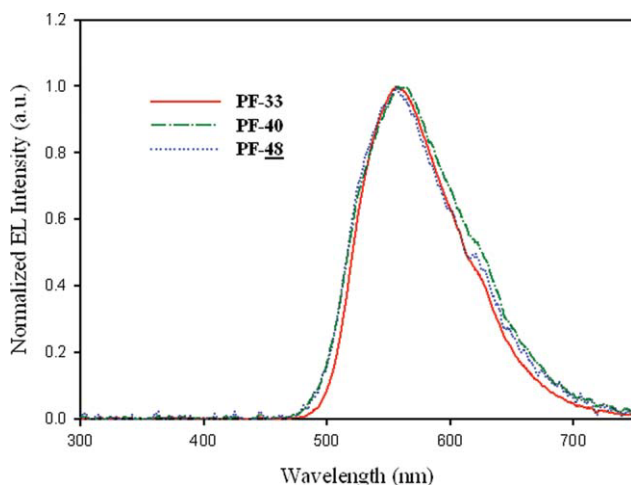


Figure 5 Electroluminescence spectra of double-layer devices using copolyfluorenes (**PF-33**, **PF-40**, or **PF-48**) as an emitting layer. Device structure: ITO/PEDOT:PSS/emitting layer/Ca/Al. The EL emission peaked at about 565 nm is originated exclusively from fluorenone units. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the device with 0.5 wt % **PF-33** is higher than those with 0.02 wt % and 1 wt % probably because of its thicker emitting layer. The maximum luminance is enhanced steadily from 610 to 4400 cd m^{-2} when **PF-33** content is increased from 0.02 to 5 wt %. The luminance efficiency reveals similar trend, that is, is increased gradually from 0.45 to 1.52 cd A^{-1} . Clearly, device performances of the blend systems are significantly improved by increasing the ratio of **PF-33**. At 5 wt % of **PF-33**, the maximum luminance and maximum luminance efficiency are 4400 cd m^{-2} and 1.52 cd A^{-1} , respectively. The performance enhancement with increasing **PF-33** contents is probably attributed to promoted electron injection because of electron-affinitive fluorenone units. Considering the intrinsic difficulty in controlling fluorenone content, especially at low concentration, blend of the copolyfluorenes having high fluorenone contents with **PF** is particularly advantageous to fabricating emitting layers with low fluorenone concentration.

Figure 6 shows the EL spectral variations of the blend devices with **PF-33** contents (0.02, 0.5, 1, and 5 wt %). The emission of fluorene segments around 420 nm degenerates quickly with increasing **PF-33** contents and almost disappears at 5 wt % **PF-33**. Therefore, the 1931 CIE chromaticity coordinates vary gradually from (0.31, 0.38) to (0.39, 0.54) with an increase in **PF-33** contents. It is interesting that the CIE coordinate of the blend device based on 0.02 wt % **PF-33** (0.31, 0.38) closes to pure white-light (0.33, 0.33). Although white-light-emitting device based on similar system was reported in literature,²³ the emission layer was doped with extra red metal complex [Ir(HFP)₃]. The spectral variation with the addition of **PF-33** (0.02–5 wt %) can be explained by the transformation in recombination sites of electron and hole. The electron and hole recombine at either fluorene or fluorenone units at low **PF-33** contents; and the emission of fluorene segments is still observable because of incomplete energy transfer. However, at high content of **PF-33** (5 wt %), not only the probability of charges recombination at fluorenone units is increased but also the energy transfer from fluorene segments to fluorenone units is promoted greatly, leading to exclusive emission of fluorenone units around 565 nm. To summarize, EL device performance of the copolyfluorenes containing high fluorenone chromophore is readily modified by simple blending with polyfluorene.

CONCLUSIONS

We have successfully prepared copolyfluorenes (**PF-40-PF-60** and **PF-33, PF-40**) containing high compositions of electron-withdrawing fluorenone moiety. The PL peaks were located at 566–568 nm (major) and 420 nm (minor) in chloroform, and at 562–564 nm in film state. Both LUMO and HOMO levels were slightly lowered with an increase in fluorenone contents. The electrochemical band gaps (E_g^{el} : 2.66–2.67 eV) were smaller than optical band gaps (2.92–3.00 eV). The performances of double-layer EL devices [ITO/PEDOT:PSS/**PF-33** + **PF**/Ca/Al] were significantly enhanced depending on the contents of

TABLE III
Optoelectronic Properties of EL Devices Based on Blends of **PF-33** and **PF**^a

wt % of PF-33 in blend	Turn-on Voltage (V)	Maximum Luminance (cd m^{-2})	CIE Coordinates (x, y) ^b	Maximum Luminance efficiency (cd A^{-1})
0.02 wt %	9.2	610	(0.31, 0.38)	0.45
0.5 wt %	18	720	(0.37, 0.51)	0.67
1 wt %	10.8	3821	(0.39, 0.53)	1.45
5 wt %	12.7	4400	(0.39, 0.54)	1.52

^a Device configuration: ITO/PEDOT:PSS/**PF** + **PF-33**/Ca/Al.

^b The CIE coordinates were estimated at maximum luminance.

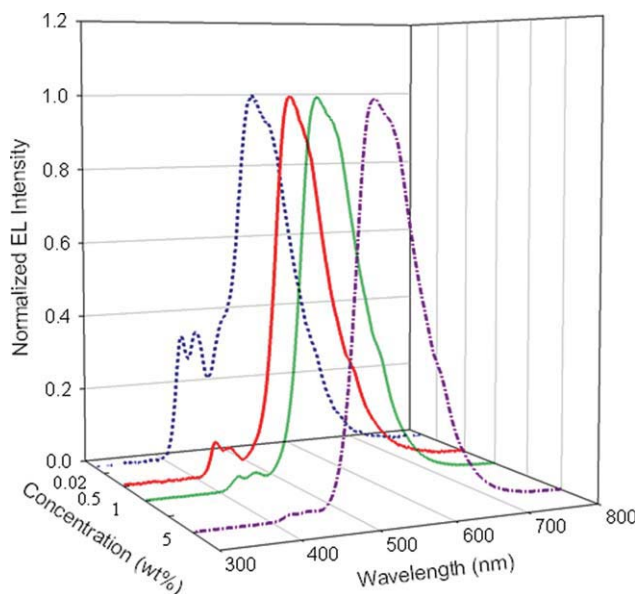


Figure 6 Influence of weight percent of PF-33 on the electroluminescence spectra of double-layer devices using blends of PF-33 and PF as emitting layer; device structure: ITO/PEDOT:PSS/PF-33 + PF/Ca/Al. Content of PF-33: (●●●●●): 0.02 wt %, (—): 0.5 wt %, (—): 1 wt %, (●—●—●—●): 5 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PF-33 (fluorenone fraction: 0.37). The maximum luminance and maximum luminance efficiency were improved from 610 cd m^{-2} to 4400 cd m^{-2} and 0.45 cd A^{-1} to $1.52 \text{ cd}^{-1}\text{A}$, respectively, when the ratios of PF-33 were increased from 0.02 wt % to 5 wt %; moreover, the CIE coordinates of the emission were varied gradually from (0.31, 0.38) to (0.39, 0.54). The EL spectra of the devices were exclusively attributed to fluorenone moiety (565 nm) at 5 wt % PF-33 because of effective charge recombination in fluorenone units and/or efficient energy transfer. Current results demonstrate that the copolyfluorenes with high fluorenone contents can be easily blended with polyfluorene to obtain efficient light-emitting materials.

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