

# Synthesis of Thermal-Stable and Photo-Crosslinkable Polyfluorenes for the Applications of Polymer Light-Emitting Diodes

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**ABSTRACT:** Three polyfluorene derivatives which have oxetane-containing phenyl group at C-9 position were synthesized via the palladium-catalyzed Suzuki-coupling reaction. The synthesized polymers PFB, PFG, and PFR emit blue, green, and red light, respectively. A double-layer device with the configuration of ITO/PEDOT/polymer/Ca/Al using PFB as the active layer showed a threshold voltage of 5 V, a maximum brightness of 2030 cd/m<sup>2</sup>, and a maximum current efficiency of 0.35 cd/A. Using PFG as the active layer, the device exhibited a threshold voltage of 6 V, a maximum brightness of 6447 cd/m<sup>2</sup>, and a maximum current efficiency of 1.27 cd/A. Using PFR as the active layer, the device showed a threshold voltage of 4 V, a maximum brightness of 2135 cd/m<sup>2</sup>, and a maximum current

efficiency of 0.16 cd/A. Better electroluminescent performance was also found based on different design of device structures. Due to photo-crosslinking property of oxetane groups, the UV-exposed thin films are insoluble in common organic solvents. A device comprised of blue, green, and red-emissive pixels was successfully fabricated by spin-coating and photo-lithographic processes. In addition, a white light-emitting device with CIE coordinate of (0.34, 0.33) was achieved by blending PFR into a host material PFB as the active layer. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 516–524, 2010

**KEYWORDS:** conjugated polymers; fluorescence; photopolymerization; PLED

**INTRODUCTION** Conjugated polymers have received broad interest recently in academic as well as in industrial research communities.<sup>1</sup> These polymer materials represent promising technology for large, flexible, and lightweight device applications, such as polymer light-emitting diode (PLED),<sup>2</sup> organic thin-film transistor (OTFT),<sup>3</sup> and photovoltaic cell.<sup>4</sup> The PLED device was first demonstrated by the Cambridge group in 1990 by using poly(*p*-phenylenevinylene) (PPV) as emitting layer.<sup>5</sup> The  $\pi$ - $\pi^*$  transitions of conjugated polymers with aromatic and/or heterocyclic units generally lead to the optical band gap with an absorption peak of 300–600 nm.<sup>6</sup> The color purity, quantum efficiency (QE) of light emission, turn-on voltage, and stability of the devices must be optimized for PLEDs to be applicable to commercial light-emitting devices. A large number of electroactive- and photoactive-conjugated polymers have been introduced during the past few years,<sup>7</sup> such as PPV,<sup>8</sup> poly(*p*-phenylene) (PPP),<sup>9</sup> polythiophene (PT),<sup>10</sup> and polyfluorene (PF).<sup>11</sup>

PFs, with their high photoluminescence (PL) and electroluminescence (EL) efficiencies are among the most promising candidates as blue light-emitting polymers.<sup>12,13</sup> PFs can also be used as host material for internal color conversion<sup>14,15</sup> and polarized light emission<sup>16,17</sup> for exploiting the liquid crystalline nature of most of the PFs. Although PFs serve as excellent materials for light-emitting application,

the so-called keto effect usually occurs with alkyl chains at the C-9 position,<sup>18,19</sup> which brings some drawbacks. The keto-defect form at higher temperatures or under long-term bias operation. The formation of fluorenone produces an additional emission band at longer wavelengths around 540 nm and changes the emissive color of the original PF. Besides, the aggregate/excimer formation also reduces device performance. Several modifications were proposed to reduce the aggregation and keto effect. The introduction of a spiro structure at the C-9 position is an effective design to suppress keto defect.

The fabrication of PLEDs by processing the active materials from solution promises to be less expensive than that of OLEDs, where deposition of the active layers requires the use of vacuum technology. The solution process used in PLEDs has three approaches. The first approach is spin coating which can easily produce large size devices with low cost. However, pixelated matrix displays are difficult to fabricate because of solution mixing problem. The second approach is ink-jet printing which is promising manufacture multicolor display.<sup>20</sup> In the other way, the wettability of the substrate has to be preadjusted (patterned by photoresist technique) to place the drops at the precise location (wetting of pixel, but not of bank). Often inhomogeneous films are obtained after drying. The third approach is photo-

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lithography. By choosing suitable photo-crosslinking groups into polymer chain and mask designed, the light-emitting polymer can be crosslinked photochemically to produce insoluble polymer networks in desired areas.<sup>21</sup>

In this article, we demonstrate the synthesis and characterization of three fluorene-based copolymers containing pendant oxetane groups. The thermal, electrochemical, optical, and other relevant physical properties of the synthesized polymers were systematically studied. Double-layer PLED devices with the configuration of ITO/PEDOT/polymer/Ca/Al were also fabricated to study their device performance. Because of the photoresist-type properties, a PLED prototype with three emission colors on one substrate was successfully fabricated.

## EXPERIMENTAL

### Characterization Methods

FTIR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with KBr pellets. <sup>1</sup>H NMR spectra were measured with a Varian 300 MHz spectrometer. Gel permeation chromatography (GPC) data assembled from a Viscotek T50A Differential Viscometer and a LR125 Laser Refractometer and three columns in series were used to measure the molecular weights of polymers relative to polystyrene standards at 35 °C. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris Diamond DSC instrument at a scan rate of 10 °C min<sup>-1</sup>. Thermal gravimetric analysis (TGA) was undertaken on a Perkin-Elmer Pyris 1 TGA instrument with a heating rate of 10 °C min<sup>-1</sup>. UV-Vis absorption spectra were obtained with an HP 8453 diode array spectrophotometer. PL emission spectra were obtained using ARC SpectraPro-150 luminescence spectrometer.

A degassed toluene solution was used to determine the PL quantum yields ( $\phi_f$ ). The concentration was adjusted to reduce the absorbance of the solution below 0.1, and the excitation was performed at the corresponding  $\lambda_{ex,max}$ . A solution of quinine sulfate in 1 N H<sub>2</sub>SO<sub>4</sub>, which has a  $\phi_f$  of 0.546 ( $\lambda_{abs} = 365$  nm), was used as a standard. Cyclic voltammetric measurements of the material were made in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte at a scan rate of 80 mV s<sup>-1</sup>. Platinum wires were used as both the counter and working electrodes, and silver/silver ions (Ag in 0.1 M AgNO<sub>3</sub> solution, from Bioanalytical Systems, Inc.) was used as the reference electrode. Ferrocene was used as an internal standard, and the potential values were obtained and converted to vs SCE (saturated calomel electrode).

### Materials

Starting materials such as 2,7-dibromofluorene, *n*-butyllithium, and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were purchased from Aldrich. All other chemicals, reagents, and solvents were used as received from commercial sources without further purification, except tetrahydrofuran (THF) and toluene which were distilled over sodium-benzophenone and calcium hydride, respectively. The Suzuki-coupling catalyst reagent tetrakis(triphenylphosphi-

ne)palladium(0) was purchased from TCI and handled under inert argon atmosphere. The syntheses of monomers M1 and M2 are shown in Scheme 1. Monomers M3–M5 were synthesized according to the previous literatures.<sup>22–24</sup>

### Synthesis of 2,7-Dibromo-9-fluorenone (1)

To a solution of fluorenone (50 g, 0.28 mole) and FeCl<sub>3</sub> (2.28 g, 14 mmole) in CHCl<sub>3</sub> (300 mL), bromine (35 L, 0.69 mole) in CHCl<sub>3</sub> (100 mL) were slowly added. The reaction mixture was stirred at 25 °C for 48 h, and then poured into sodium thiosulfate solution (300 mL) until the red color of bromine disappeared. The organic layer was dried over MgSO<sub>4</sub>, and the solvent was removed in vacuo. The residue was purified by column chromatography (SiO<sub>2</sub>, hexane) to yield 15.71 g (81%) yellow solid, mp: 204 °C. <sup>1</sup>H NMR (300 MHz, DMSO,  $\delta$ , ppm): 7.81 (m, 4H, aromatic protons), 7.73 (s, 2H, aromatic protons).

### Synthesis of 2,7-Dibromo-9,9'-bis(4-hydroxyphenyl) Fluorene (2)

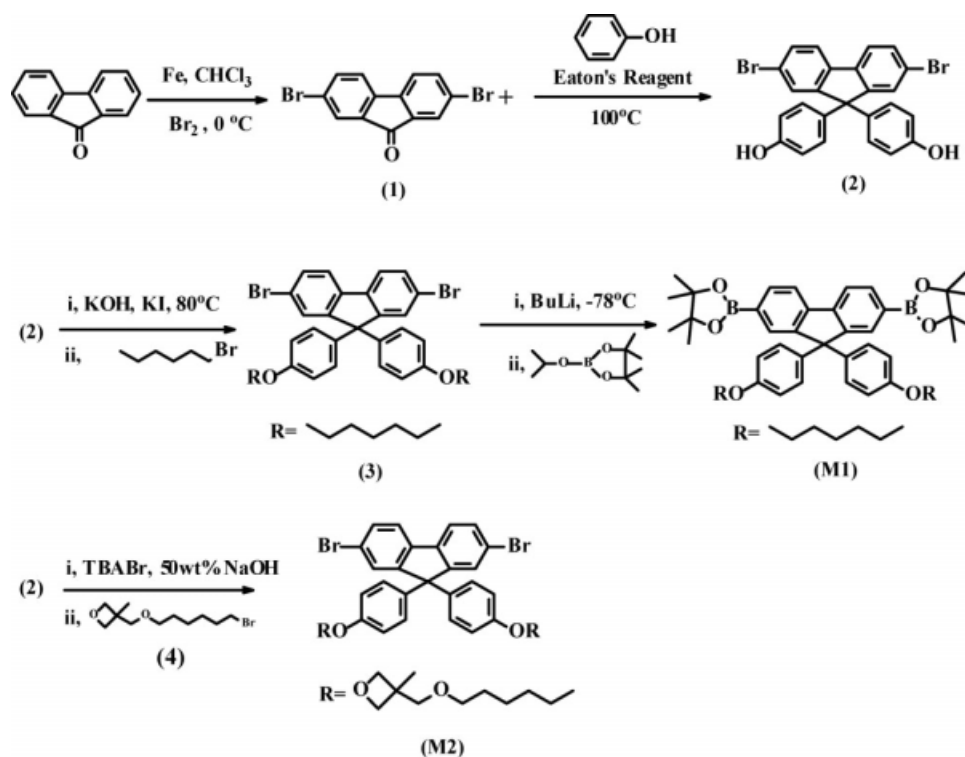
To a solution of 2,7-dibromofluorenone (5 g, 14.8 mmole) and phenol (10 g, 106.3 mmole) under nitrogen atmosphere, Eaton's reagent (70 mL) was slowly added. The reaction mixture was stirred at 100 °C for 1 h and then poured into water. The organic layer was dried over MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography (silica gel, EA:hexane = 1:3 as eluent) to yield 6.1 g (81%) white solid, mp: 59 °C. <sup>1</sup>H NMR (300 MHz, DMSO,  $\delta$ , ppm): 9.41 (s, 2H, aromatic protons), 7.89 (d, 2H, aromatic protons), 7.57 (dd, 2H, aromatic protons), 7.47 (d, 2H, aromatic protons), 6.87 (d, 4H, aromatic protons), 6.65 (d, 4H, aromatic protons).

### Synthesis of 2,7-Dibromo-9,9-di(4-hexylphenyl)-9H-fluorene (3)

To a solution of (2) (5 g, 9.84 mmole), potassium hydride (1.66 g, 29.52 mmole) and potassium iodide (0.33 g, 1.97 mmole) in acetonitrile (40 mL) was added bromohexane (4.05 g, 24.6 mmole) at 80 °C. The reaction mixture was refluxed for 24 h, and then poured into water. The organic layer was dried over MgSO<sub>4</sub>, and the solvent was removed in vacuo. The residue was purified by column chromatography (silica gel, hexane as eluent) to yield 5.3 g (89%) white solid, mp: 41 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 7.56–6.73 (m, 14H, aromatic protons), 3.91–3.86 (t, 4H, O—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>4</sub>—CH<sub>3</sub>), 2.30–1.20 (m, 16H, O—CH<sub>2</sub>—(CH<sub>2</sub>)<sub>4</sub>—CH<sub>3</sub>), 0.94–0.82 (t, 6H, —(CH<sub>2</sub>)<sub>4</sub>—CH<sub>3</sub>).

### Synthesis of 2-[9,9-Di[4-(hexyloxy)phenyl]-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-2-fluorenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (M1)

To a cooled solution (–78 °C) of (3) (5 g, 7.39 mmole) in 20 mL dry THF was added 1.6 M *n*-butyllithium/hexane (11.55 mL, 18.48 mmole) dropwise. The mixture was kept at –78 °C for and stirred 1 h. A solution of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.52 mL, 22.17 mmol) was then slowly added in 10 min and the reaction mixture was stirred overnight. After extracting with ether and water, the collected organic phase was dried over MgSO<sub>4</sub> and concentrated. The crude product was purified by recrystallization


**SCHEME 1** Synthesis of monomers M1 and M2.

from hexane to yield 3.5 g (61%) white crystals, mp: 245 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.77–6.69 (14H, aromatic ring), 3.88–3.84 (t, 4H,  $\text{O}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$ ), 1.71–1.68 (m, 16H,  $\text{O}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$ ), 1.29 (s, 24H,  $\text{CH}_3$ ), 0.86–0.84 (t, 6H,  $-(\text{CH}_2)_4-\text{CH}_3$ ).

#### Synthesis of 3-(((6-Bromohexyl)oxy)methyl)-3-methyloxetane (4)

A mixture of tetrabutylammonium chloride (TBACl) (0.5 g), hexane (120 mL), 50 wt % NaOH water solution (120 mL), dibromohexane (60.25 mL, 391.6 mmole), and 3-methyl-3-oxetanemethanol (10 g, 97.91 mmole) was stirred at room temperature for 24 h, followed by refluxing at 75 °C for additional 4 h. After cooling the reaction mixture to room temperature, the mixture was extracted with hexane and water. The organic phase was washed with saturated  $\text{NaCl}(\text{aq})$ , dried over  $\text{MgSO}_4$ , and concentrated to give the crude product. Further purification was carried out by distillation in vacuum (2 mmHg, 90 °C) to give 18.2 g (70.32 %) yellow oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.97 (s, 3H,  $-\text{CH}_3$ ), 1.26–1.76 (m, 6H,  $\text{CH}_2-(\text{CH}_2)_3-\text{CH}_2$ ), 3.26–3.36 (m, 6H,  $-\text{CH}_2-\text{O}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-\text{Br}$ ), 4.19–4.38 (m, 4H, ring protons).

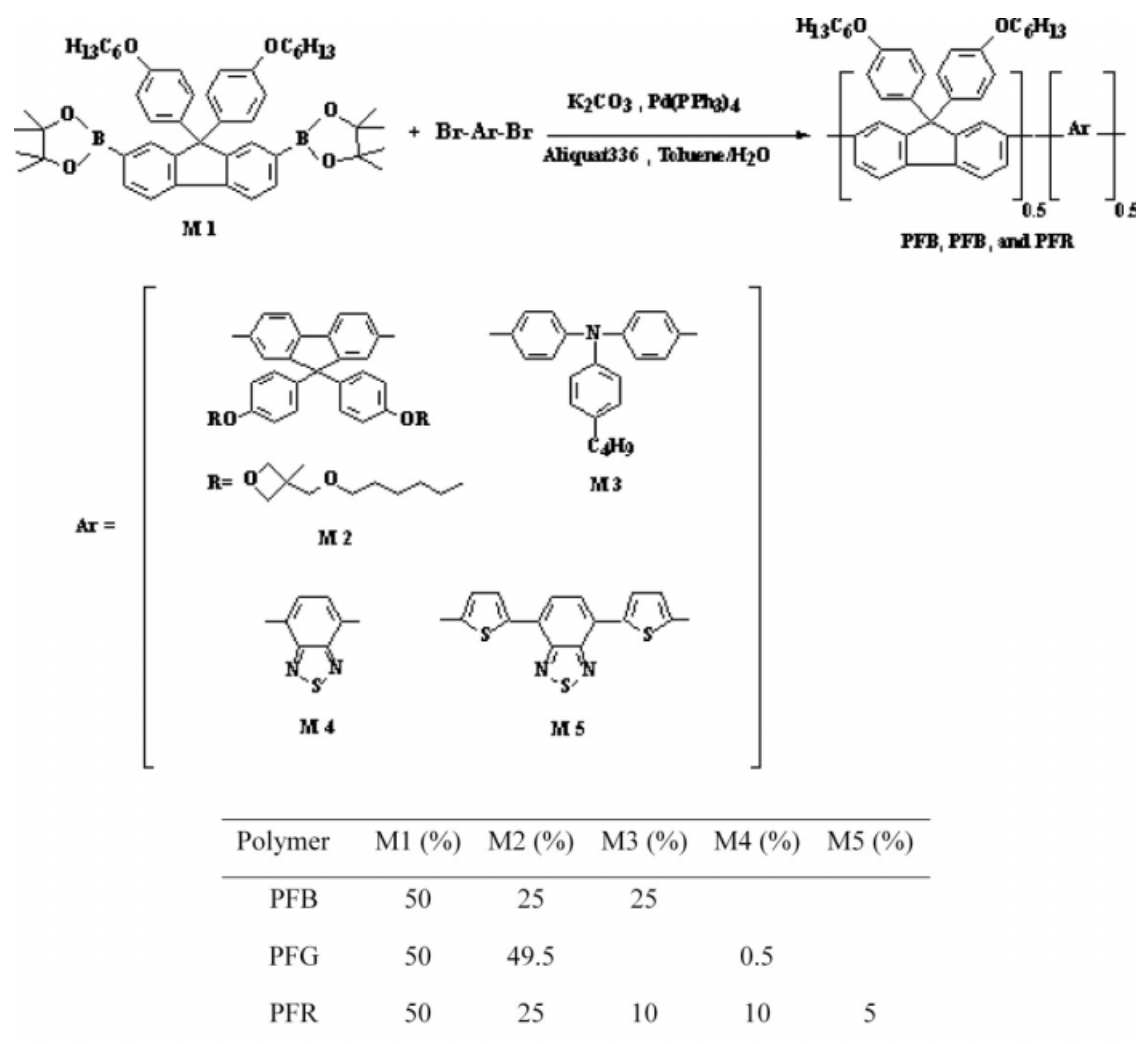
#### Synthesis of 3-(((6-(4-(3,6-Dibromo-9-[4-(((3-methyl-3-oxetanyl)methoxy)hexyl)oxy)phenyl]-9H-9-fluorenyl)-phenoxy)hexyl)methyl)-3-methyloxetane (M2)

To a solution of M1 (6.9 g, 13.58 mmole), potassium hydride (2.29 g, 40.74 mmole) and potassium iodide (0.46 g, 2.72 mmole) in acetonitrile (50 mL) was added (4) (9 g, 2.72 mmole) slowly. The reaction mixture was then refluxed for

24 h. After cooling to room temperature, the mixture was poured into water. The organic layer was dried over  $\text{MgSO}_4$  and concentrated in vacuo. The crude product was purified by column chromatography (silica gel, EA:hexane = 1:5 as eluent) to yield 9.1 g (76.4%) colorless oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.93–6.80 (m, 14H, aromatic protons), 4.33–4.14 (s, 8H, ring protons), 3.91–3.87 (t, 4H), 3.42–3.27 (m, 8H,  $-\text{CH}_2-\text{O}-\text{CH}_2$ ), 1.98–1.14 (m, 16H,  $\text{CH}_2-(\text{CH}_2)_3-\text{CH}_2$ ), 0.84–0.82 (s, 6H,  $-\text{CH}_3$ ).

#### General Synthetic Procedure for Polymers PFB, PFG, and PFR

Three polymers PFB, PFG, and PFR which emit blue, green, and red light, respectively, were prepared via palladium-catalyzed Suzuki-coupling reaction.<sup>25</sup> Scheme 2 outlines the syntheses of the three synthesized polymers. A typical synthetic procedure for PFB is given as follows. To a 50 mL two-necked round flask was added M2 (1 g, 1.07 mmole), M1 (0.59 g, 0.85 mmole), M3 (0.37 g, 0.84 mmol), and 15 mL of toluene.  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{K}_2\text{CO}_3(\text{aq})$  (2.0 M), and aliquat 336 were then added under an argon atmosphere. The mixture was refluxed with vigorous stirring at 85 °C for 4 days. *N,N*-Bis(4-methylphenyl)-*N*-(4-bromophenyl)amine and *N,N*-bis(4-methylphenyl)-*N*-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl] amine were sequentially added into the mixture and stirred for additional 6 h. After cooling to room temperature, the reaction mixture was poured into methanol to precipitate polymer which was purified by dissolving in THF and reprecipitated from methanol several times. After drying under vacuum for 24 h, the polymer was obtained as a light-green solid with yield of 62–90%.



**SCHEME 2** Synthesis of polymers PFB, PFG, and PFR.

#### Polymer PFB

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.83–2.15 (m, alkyl protons), 3.40–3.88 (m,  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ), 4.30–4.47 (m, ring protons), 6.71–7.76 (m, aromatic protons). Elemental Anal. Calcd. for  $\text{C}_{143}\text{H}_{165}\text{O}_{10}\text{N}_1$ : C, 83.87; H, 7.63; N, 0.68. Found: C, 81.11; H, 7.56; N, 0.96.

#### Polymer PFG

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.83–1.70 (m, alkyl protons), 3.40–3.86 (m,  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ), 4.30–4.47 (m, ring protons), 6.71–7.73 (m, aromatic protons). Elemental Anal. Calcd. for  $\text{C}_{4179.5}\text{H}_{4973}\text{O}_{397}\text{N}_{10.5}$ : C, 81.76; H, 7.84; N, 0.02. Found: C, 78.94; H, 7.57; N, 0.66.

#### Polymer PFR

$^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 0.71–1.70 (m, alkyl protons), 3.40–3.86 (m,  $-\text{CH}_2-\text{O}-\text{CH}_2-$ ), 4.30–4.47 (m, ring protons), 6.71–7.71 (m, aromatic protons). Elemental Anal. Calcd. for  $\text{C}_{338.5}\text{H}_{390}\text{O}_{25}\text{N}_4\text{S}_{2.5}$ : C, 81.80; H, 7.41; N, 1.13. Found: C, 79.77; H, 7.33; N, 1.45.

#### Device Fabrication

Double-layer devices were fabricated as sandwich structures between calcium (Ca) cathodes and indium tin oxide (ITO) anodes. ITO-coated glass substrates were cleaned sequentially in ultrasonic baths of detergent, 2-propanol/deionized water (1:1 volume) mixture, toluene, deionized water, and acetone. A 50 nm-thick hole injection layer of poly(ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) was spin-coated on top of ITO from a 0.7 wt % dispersion in water and dried at 150 °C for 1 h in a vacuum. Thin films of synthesized polymers were spin-coated from toluene solutions onto the PEDOT layer and dried at 100 °C for 1 h in a vacuum. The polymer solution contains diphenyliodonium hexafluoroarsenate (6 wt %) as photo initiator. The thickness of the active layer was ~50 nm. The active layer was irradiated (standard handheld UV lamp,  $\lambda = 302$  nm) for about 20 s in inert gas atmosphere at room temperature. Afterward, to further advance the crosslinking process in the growing network, the active layer was annealed at 120 °C for 30 min. The active layer was rinsed with THF and finally heated to 120 °C for 15 min to remove radical cations

**TABLE 1** Average Molecular Weights and Thermal Properties of Polymers PFB, PFG, and PFR

Polymer	$M_n$ ( $\times 10^4$ ) <sup>a</sup>	$M_w$ ( $\times 10^4$ )	PDI	$T_d$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	$T_g$ ( $^{\circ}\text{C}$ ) <sup>c</sup>
PFB	1.0	1.2	1.15	371	90
PFG	1.85	3.42	1.8	385	102
PFR	2.2	2.44	1.11	399	83

<sup>a</sup> Determined by GPC by eluting with THF, by comparison with polystyrene standards.

<sup>b</sup> Temperature at which a 5% weight loss occurred was determined at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  under a nitrogen atmosphere.

<sup>c</sup> The value of  $T_g$  was determined at a heating rate of 20  $^{\circ}\text{C}/\text{min}$  under a nitrogen atmosphere.

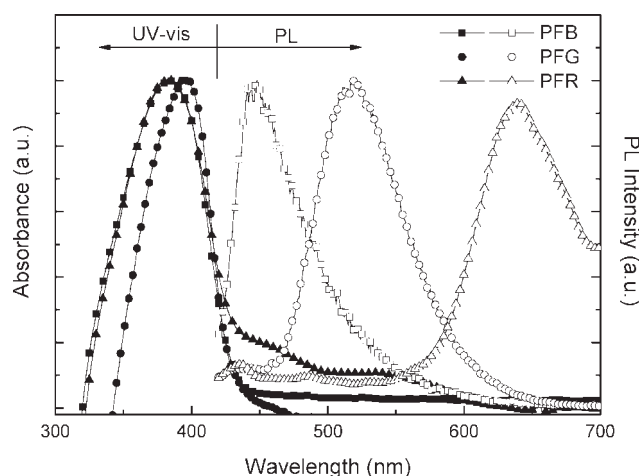
formed upon polymerization. The resulting polymer networks were found to be insoluble in any common solvent. Finally, 35 nm Ca and 100 nm Al electrodes were made through a shadow mask onto the polymer films by thermal evaporation using an AUTO 306 vacuum coater (BOC Edwards, Wilmington, MA). Evaporations were carried out typically at base pressures lower than  $8 \times 10^{-7}$  torr. The active area of each EL device was 4 mm<sup>2</sup>.

### Synthesis and Characterization

The monomers M1 and M2 containing two phenyl groups at C-9 position instead of alkyl chain were designed to suppress the keto effect. Triphenylamine(TPA) compounds are well-known hole-transporting materials. TPA-containing monomer M3 was introduced to fine-tune the EL emission wavelength of polyfluorenes in the range 450–470 nm and substantially improve the EL performance. Monomer M4 containing benzo-thiodiazole (BTDZ) structure was incorporated and yellow-green light was emitted via energy transfer from fluorene to BTDZ moiety. Monomer M5 containing BTDZ and two additional thiophene rings to elongate the conjugated length and thus the emitting wavelength can be further shifted to red light region. The chemical structures of the resulting polymers were confirmed by <sup>1</sup>H NMR and elemental analyses. The actual ratio calculated from elemental analyses of C, H, and N was in good agreement with the feeding ratios of the monomers. Slight deviations might be caused by two end-capping reagents (*N,N*-bis(4-methylphenyl)-*N*-(4-bromophenyl) amine and *N,N*-bis(4-methylphenyl)-*N*-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl] amine. The obtained polymers are completely soluble in common organic solvents, such as toluene, THF, and chloroform. The average molecular weights are summarized in Table 1. It can be seen that  $M_n$  and  $M_w$  values of these polymers are in the range from  $1.0 \times 10^4$  to  $2.2 \times 10^4$  and from  $1.2 \times 10^4$  to  $3.42 \times 10^4$ , respectively, with polydispersity index less than 2.

### Thermal Properties

Thermal stability of conjugated polymers is an important factor for PLED application, which is generally evaluated by DSC and TGA techniques. The thermal decomposition temperatures ( $T_d$ , 5% weight loss) and the glass transition temperatures ( $T_g$ ) of three polymers are also listed in Table 1. All three polymers show a  $T_g$  value above 80  $^{\circ}\text{C}$ , which is


**FIGURE 1** UV-Vis absorption and PL spectra of polymers PFB, PFG, and PFR in thin-film state.

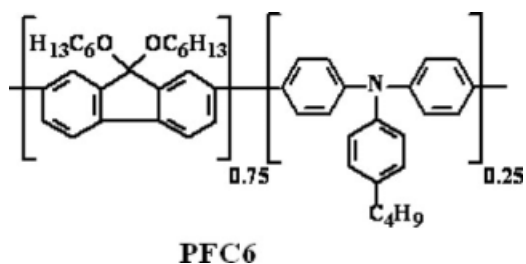
higher than that of poly(9,9-dioctylfluorene) ( $T_g = 51$   $^{\circ}\text{C}$ ).<sup>26</sup> It is well-known that high  $T_g$  value is essential for polymers to be used as emissive materials. In addition, these polymers also exhibit high  $T_d$  value over 380  $^{\circ}\text{C}$ , indicating good potential use in light-emitting devices.

### Optical Properties

The fluorescent behavior of a polymer fundamentally depends on the band gap between the HOMO and LUMO, which depends on delocalization of  $\pi$ -electrons along the polymer backbone. The characteristic peak in the emission spectrum arises as an excited electron relaxes into vibronic energy level of the HOMO. The optical spectra of conjugated polymers are usually broad, which is due to the coupling of several different vibronic modes. Figure 1 shows the normalized UV-Vis absorption and PL spectra of three polymers in thin-film state. The wavelengths of UV-Vis absorption and PL emission maxima of these polymers in dilute toluene solution ( $10^{-5}$  M) and in film state are summarized in Table 2. The absorptions located in the range from 381 to 387 nm were due to  $\pi$ - $\pi^*$  transition of conjugated backbones. For polymers PFB and PFG, no shoulder peak in UV-Vis absorption region was observed. For polymer PFR, two slight shoulders (460 and 525 nm) were found, resulting from the BTDZ and thiophene-BTDZ-thiophene moieties. The blue emission of polyfluorene around 440 nm could be effectively quenched by introducing BTDZ group into the polymer main chain, tuning emission to green light region around 517 nm. It also reveals the effective energy transfer from photo-

**TABLE 2** Optical Properties of Polymers PFB, PFG, and PFR

Polymer	UV( $\lambda_{\text{max}}$ (nm))		PL( $\lambda_{\text{max}}$ (nm))		PL <sub>eff</sub> (%)
	Toluene	Film	Toluene	Film	
PFB	380	383	442	448	88
PFG	387	395	419 (440)	517	87
PFR	381	382	526 (627)	640	23



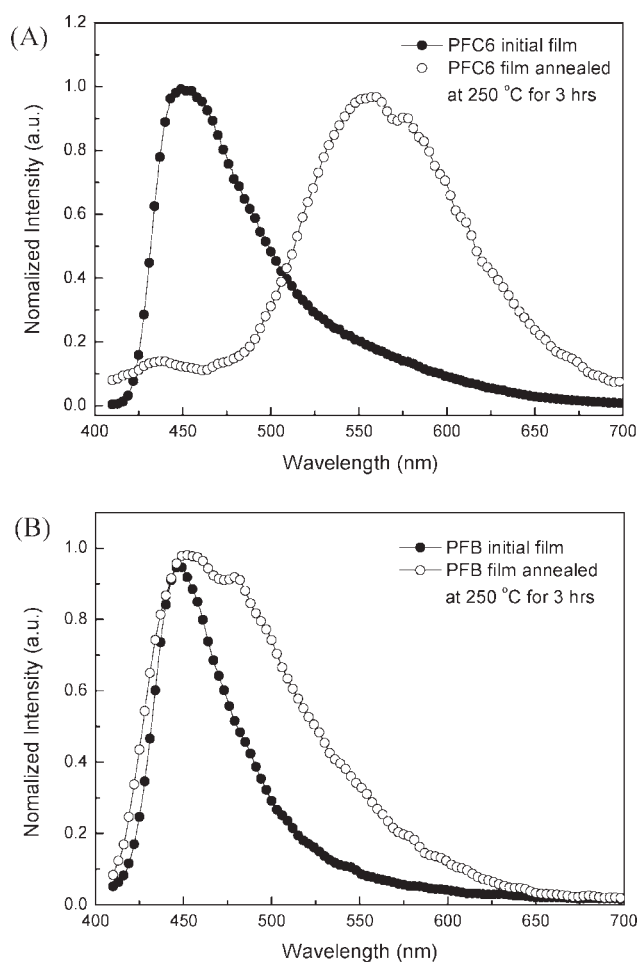
**CHART 1** Chemical structure of PFC6.

generated excitons on the polyfluorene segment to BTMZ groups. By incorporating thiophene-BTDMZ-thiophene moieties into polymer main chains, PL emission was further red-shifted to 640 nm in thin-film state. Table 2 also outlines the PL quantum efficiencies of three polymers as measured by an integrating sphere. These polymers exhibit moderate PL QE values from 23 to 87% in toluene solution.

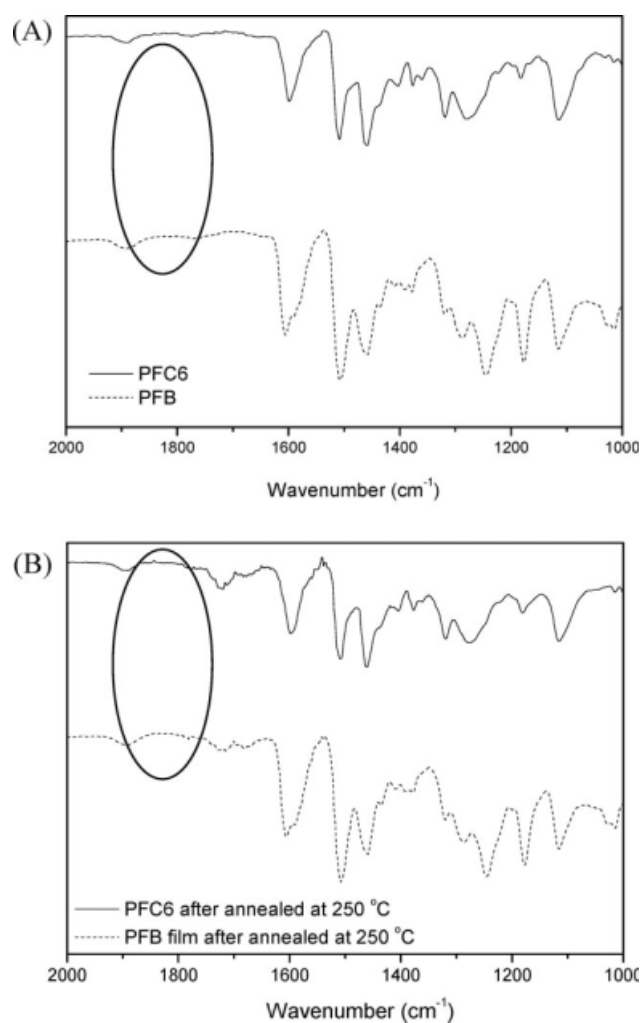
### Annealing Experiment

According to the previous literature,<sup>27</sup> when the temperature inside PLED devices exceeds 86 °C under a high forward-

bias condition, the optical properties, especially luminescence efficiency and color stability of light-emitting material are strongly affected. PLED devices using polyfluorene as light-emitting layer usually show a green emission under a high forward-bias condition. The origin of the green emission in polyfluorene-based conjugated polymers has been mostly attributed to aggregation and/or excimer formation or keto defects caused from the formation of fluorenone units in the PF backbone.<sup>28–31</sup> The utility of polyfluorenes is thus limited because of the tendency to undergo interchain aggregation. Furthermore, when the solid films of the polymers are maintained under the higher temperature above  $T_g$ , the keto-defect would appear and emit green light around 550 nm. This is because the fluorenone group exhibits lower energy band gap and the energy transfer from fluorenyl ring to fluorenone moiety is very efficient. To investigate the thermal stability and the keto effect of the prepared polymers, thin films were annealed at 250 °C in air for 3 h. For comparison, a known polyfluorene derivative PFC6 without phenyl ring at C-9 position of fluorene ring was also prepared and tested. The chemical structure of PFC6 is shown in Chart 1.



**FIGURE 2** PL spectra of polymers (A) PFC6 and (B) PFB in thin-film state before and after annealing at 250 °C for 3 h in air.



**FIGURE 3** FTIR spectra of polymers PFC6 and PFB (A) at 25 °C (B) after annealing at 250 °C for 3 h.

**TABLE 3** Electrochemical Properties of PFB, PFG, and PFR

Sample	Optical Band Gap <sup>a</sup> (eV)	$E_{\text{ox.onset}}^b$ (eV)	$E_{\text{red.onset}}^b$ (eV)	HOMO <sup>c</sup> (eV)	LUMO <sup>c</sup> (eV)
PFB	2.85 (435)	1.35	-1.5	-5.75	-2.9
PFG	2.85 (435)	1.37	-1.48	-5.77	-2.92
PFR	1.87 (663)	1.39	-0.48	-5.79	-3.92

<sup>a</sup> The optical band gap estimated from the onset wavelength (value in parentheses) of UV-Vis spectra of the polymer film.

<sup>b</sup> The  $E_{\text{ox}}$  and the  $E_{\text{red}}$  are the onset potentials of oxidation and reduction, respectively.

<sup>c</sup> Calculated from the empirical formula,  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.40)$  (eV),  $E_{\text{LUMO}} = -(E_{\text{red}} + 4.40)$  (eV).

Figure 2(A,B) shows the normalized photoluminescence (PL) spectra of polymers PF1 and PFB films at room temperature and thermally annealed at 250 °C for 3 h. In Figure 2(A), the PFC6 film annealed at 250 °C for 3 h showed a strong green emission at a longer wavelength of about 559 nm, which is attributed to the fluorenone emission when compared with the fresh films with max emission  $\lambda_{\text{max}}$  band located at 448 nm. Turning to polymer PFB, the PL spectrum of PFB showed a shoulder around 500 nm under similar heating conditions. However, the max emission  $\lambda_{\text{max}}$  remained at 448 nm, suggesting better thermal stability against annealing process. It is generally thought that defect phenomena are generally appeared for those alkyl-substituted polyfluorene, such as PFC6. This unchanged PL curve of polymer PFB strongly hints that polyfluorene with phenyl group attached at C-9 position may inhibit the aggregation of polymer chains. Figure 3 shows the FTIR spectra of PF1 and PFB films after annealed at 250 °C for 3 h. No obvious fluorenone (C=O) characteristic IR peak at around 1720  $\text{cm}^{-1}$  peak was found for PFB. The above observations suggest that incorporation of phenyl group at C-9 position could effectively suppress the keto formation and aggregation of polymer chains.

### Electrochemical Properties

The electrochemical behaviors of these polymers were investigated by cyclic voltammetry (CV). The corresponding highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy levels were estimated from the onset of the redox potentials. HOMO and LUMO energy levels of the chromophores were calculated according to empirical formulae  $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4)$  (eV) and  $E_{\text{LUMO}} = -(E_{\text{red}} + 4.4)$  (eV).<sup>32</sup> From the difference of the onset potentials and the optical band gaps (Eg) calculated from the onsets of UV absorption spectra, the energy levels, the oxidation, and reduction potentials were determined and are summarized in Table 3. Polyfluorenes usually show an onset in oxidation curve around 1.4 V, which can be assigned to the p-doping potential of polyfluorene main chains. Mean-

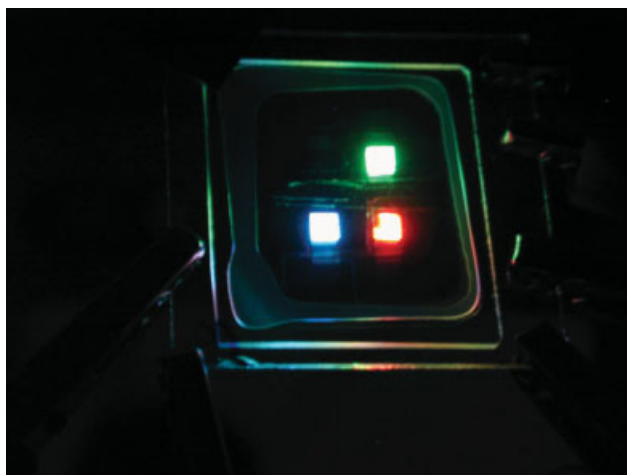
while, the electrochemical oxidation of polymers exhibit peak at 1.8 V versus Ag/Ag<sup>+</sup>, and the characteristic peak is originated from phenyl-fluorene units. However, the BTMZ moiety in polymers PFG and PFR is more electron-deficient and easier to be reduced when compared with PFB. Since BTMZ has a smaller gap than polyfluorene, the excitation energy on the fluorene segments can be transferred to BTMZ unit efficiently. For PFR, the HOMO and LUMO energy levels were shifted lower because of adding two thiophene groups on both sides of BTMZ moiety. The incorporation of thiophene-BTMZ-thiophene moiety onto polymer chains increases the conjugated length and reduces the optical band gap as well.

### Electroluminescent Properties

The EL properties of the copolymers were investigated using a double-layer device with the configuration of ITO/PEDOT/polymer/Ca/Al. The maximum EL emission bands and CIE'1931 coordinates of the three devices were recorded in Table 4. It is clear that PFB, PFG, and PFR devices emitted blue, green, and red light as expected. The turn-on voltage is measured to be 4–5 V. The PFB device showed a maximum brightness of 2030  $\text{cd/m}^2$  (at 12 V) and a maximum current efficiency of 0.35  $\text{cd/A}$  (303  $\text{mA/cm}^2$ ). The PFG device revealed a maximum brightness of 6447  $\text{cd/m}^2$  (at 11 V) and a maximum current efficiency of 1.27  $\text{cd/A}$  (507  $\text{mA/cm}^2$ ). The PFR device showed a maximum brightness of 2135  $\text{cd/m}^2$  (at 13 V) and a maximum yield of 0.16  $\text{cd/A}$  (1334  $\text{mA/cm}^2$ ). It is worthy to note that PFB and PFR devices emitted deep blue and red light, from CIE'1931 coordinates of (0.15, 0.14) and (0.68, 0.32), respectively. Since these light-emitting polymers contain photo-crosslinkable oxetane groups, photo-lithography process was substantially investigated to obtain blue, green, and red pixelated devices. For this purpose, organic layers were irradiated by UV light through a shadow mask. After curing, the films were developed by immersing them into THF to dissolve nonirradiated part. By sequentially developing green, blue, and red part through photo-lithographic process, three different light

**TABLE 4** Device Performance of Polymers PFB, PFG, and PFR

Polymer	Turn-On Voltage (V)	Max Brightness, $\text{cd/m}^2$ @ V	Yield <sub>max</sub> , $\text{cd/A}$	EL Spectrum, $\lambda_{\text{max}}$ (nm)	CIE 1931 (x, y)
PFB	5	2,030	0.35	450	(0.15, 0.14)
PFG	6	6,447	1.27	520	(0.28, 0.49)
PFR	4	2,135	0.16	656	(0.68, 0.32)

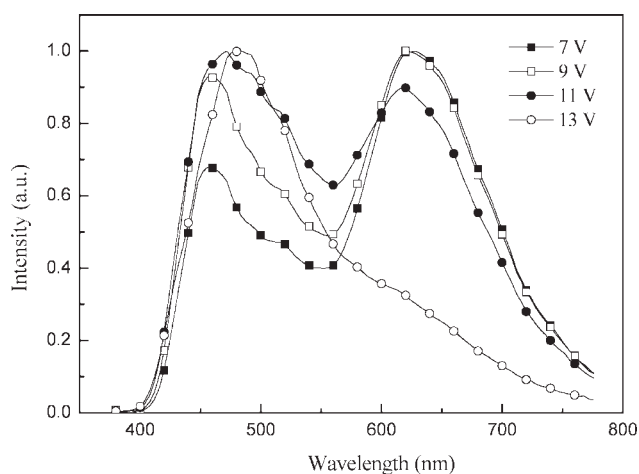


**FIGURE 4** Photograph of an RGB (red, green, blue) device. Dimensions of the pixels are  $20 \times 20$  (mm  $\times$  mm).

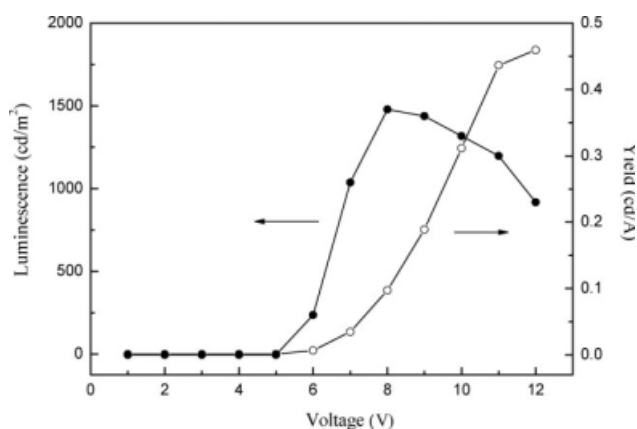
emitted on the same substrate was successfully achieved, as shown in Figure 4.

### White Polymer Light-Emitting Diode

White light organic light-emitting devices (WOLEDs) have attracted a lot of interest because of their potential applications in solid-state-lighting, maskless full color OLED fabrication with color filter, as well as backlights for liquid crystal displays. Here, we present an easy and effective way to produce white light PLED devices by blending method. Blue light-emitting PFB was used as host matrix, while 2% PFR was selected as guest material. A similar double-layer device with the configuration of ITO/PEDOT/98% PFB + 2% PFR/Ca/Al was fabricated. Pure white light with CIE'1931 coordinate (0.34, 0.33) was revealed under bias operation of 11 V. Figure 5 shows the EL emission spectra of the device under different voltage. It should be noted that the device emitted dominate red light at lower voltage of 7 V and blue light at



**FIGURE 5** EL spectra of the device: ITO/PEDOT/blend of PFB, PFG, and PFR/Ca/Al at the different voltages.



**FIGURE 6** I-V-L curves of the device with ITO/PEDOT/blend of PFB, PFG, and PFR/Ca/Al configuration.

higher voltage over 13 V. Figure 6 depicts luminance-voltage-current efficiency characteristics of the device, showing a maximum brightness of  $1500 \text{ cd/m}^2$  and a maximum current efficiency of  $0.46 \text{ cd/A}$ .

### CONCLUSIONS

In conclusion, three oxetane-containing polyfluorene derivatives which emit blue, green, and red light were synthesized and characterized. FTIR and PL spectral experiments demonstrate that the incorporation of the phenyl group at C-9 position of fluorene moiety could effectively suppress the keto-defect. Because of the photo-crosslinking property of oxetane groups, the UV-exposed thin films are not soluble in common organic solvents. A device containing blue, green, and red-emissive pixels was fabricated by spin-coating and photo-lithography processes. In addition, a pure white light-emitting device was demonstrated by blending 2% PFR into host materials PFB as the active layer, with CIE coordinate of (0.34, 0.33).

### REFERENCES AND NOTES

- 1 Heeger, A. J. *Solid State Commun* 1998, 107, 673–679.
- 2 Ziemelis, K. *Nature* 1999, 399, 408–411.
- 3 Dang, T. T. M.; Park, S. J.; Park, S. J.; Park, J. W.; Chung, D. S.; Park, C. E.; Kim, Y. H.; Kwon, S. K. *J Polym Sci Part A: Polym Chem* 2007, 45, 5277–5284.
- 4 Bundgaard, E.; Krebs, F. C. *Sol Energy Mater Sol Cells* 2007, 91, 954–985.
- 5 Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* 1990, 347, 539–541.
- 6 Kim, D. Y.; Cho, H. N.; Kim, C. Y. *Prog Polym Sci* 2000, 25, 1089–1139.
- 7 Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew Chem Int Ed* 1998, 37, 402–428.



- 8** Chen, K. B.; Chen, M. H.; Yang, S. H.; Hsieh, C. H.; Hsu, C. S.; Chen, C. C.; Chieh, H. J. *J Polym Sci Part A: Polym Chem* 2006, 44, 5378–5390.
- 9** Kranzelbinder, G.; Leising, G. *Rep Prog Phys* 2000, 63, 729–762.
- 10** Pei, J.; Yu, W. L.; Ni, J.; Lai, Y. H.; Huang, W.; Heeger, A. J. *Macromolecules* 2001, 34, 7241–7248.
- 11** Kameshima, H.; Nemoto, N.; Endo, T. *J Polym Sci Part A: Polym Chem* 2001, 39, 3143–3150.
- 12** Pei, Q.; Yang, Y. *J Am Chem Soc* 1996, 118, 7416–7417.
- 13** Leclerc, M. *J Polym Sci Part A: Polym Chem* 2001, 39, 2867–2873.
- 14** Virgili, T.; Lidzey, D. G.; Bradley, D. D. C. *Adv Mater* 2000, 12, 58–62.
- 15** Lane, P. A.; Palilis, L. C.; O'Brien, D. F.; Giebeler, C.; Cadby, A. J.; Lidzey, D. G.; Campbell, A. L.; Blau, W.; Bradley, D. D. C. *Phys Rev B* 2001, 63, 235206-1–8.
- 16** Oda, M.; Nothofer, H.-G.; Lieser, G.; Scherf, U.; Meskers, S. C. J.; Neher, D. *Adv Mater* 2000, 12, 362–365.
- 17** Contoret, A. E. A.; Farrar, S. R.; Jackson, P. O.; Khan, S. M.; May, L.; O'Neill, M.; Nicholls, J. E.; Kelly, S. M.; Richards, G. J. *Adv Mater* 2000, 12, 971–974.
- 18** Scherf, U.; List, E. J. W. *Adv Mater* 2002, 14, 477–487.
- 19** Wu, F. I.; Reddy, D. S.; Shu, C. F.; Liu, M. S.; Jen, A. K.-Y. *Chem Mater* 2003, 15, 269–274.
- 20** Gans, B.-J. G.; Duineveld, P. C.; Schubert, U. S. *Adv Mater* 2004, 16, 203–213.
- 21** Müller, C. D.; Falcou, A.; Reckefuss, N.; Rojahn, M.; Wiederhahn, V.; Rudati, P.; Frohne, H.; Nuyken, O.; Becker, H.; Meerholz, K. *Nature* 2003, 421, 829–833.
- 22** Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* 1997, 30, 7686–7691.
- 23** Millard, I. S. *Synth Met* 2000, 111, 119–123.
- 24** Pilgram, K.; Zupan, M.; Sliles, R. *J Heterocycl Chem* 1970, 7, 629–633.
- 25** Miyaura, N.; Suzuki, A. *Chem Rev* 1995, 95, 2457–2483.
- 26** Ding, J.; Day, M.; Robertson, G.; Roovers, J. *Macromolecules* 2002, 35, 3474–3483.
- 27** Zhou, X.; He, J.; Liao, L. S.; Lu, M.; Ding, X. M.; Hou, X. Y.; Zhang, X. M.; He, X. Q.; Lee, S. T. *Adv Mater* 2000, 12, 265–269.
- 28** Gaal, M.; List, E. J. W.; Scherf, U. *Macromolecules* 2003, 36, 4236–4237.
- 29** Bliznyuk, V. N.; Carter, S. A.; Scott, J. C.; Klärner, G.; Miller, R. D.; Miller, D. C. *Macromolecules* 1999, 32, 361–369.
- 30** Pei, J.; Yu, W. L.; Huang, W.; Heeger, A. J. *Chem Commun* 2000, 1631–1632.
- 31** Yu, W. L.; Pei, J.; Cao, Y.; Huang, W.; Heeger, A. J. *Chem Commun* 1999, 1837–1838.
- 32** Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth Met* 1997, 87, 53–59.