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Polyfluorenes Containing Tetraphenylthiophene Segments: Synthesis, Photophysics, and Electroluminescence

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ABSTRACT: 2,5-Bis(4-bromophenyl)-3,4-diphenylthiophene was synthesized from benzyl chloride and sulfur and through the subsequent bromination of the intermediate 2,3,4,5-tetraphenylthiophene. It was condensed with 2,7-dibromo-9,9-dihexylfluorene via a nickel-mediated Yamamoto coupling reaction to afford a new series of statistical copolymers with various compositions. In addition, poly(9,9-dihexylfluorene) (PF) was synthesized under the same conditions for comparison. All the polymers were soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, and dichloromethane. Their glass-transition temperatures increased with an increase in the tetraphenylthiophene (TPT) content in the polymers, and they were 63–149 °C. The solutions of the polymers in THF emitted intense blue light with a photoluminescence maximum at 418–440 nm and quantum yields of 0.32–0.62. Thin films of the polymers with TPT fractions lower than 20 mol % emitted blue-green light with two well-resolved peaks at 445 and 520 nm and an optical band gap of about 2.85 eV. A thin film of the polymer with a TPT fraction of 50 mol % emitted pure blue light with a maximum at 419 nm and an optical band gap of 3.28 eV. An enhancement of the light-emitting-diode brightness by a factor of ~ 8 with respect to that of PF was achieved in a polymer containing 5 mol % TPT. © 2006 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 44: 4015–4026, 2006

Keywords: conjugated polymers; light-emitting diodes (LEDs); photophysics; polyfluorenes; synthesis

INTRODUCTION

Over the past years, a large research effort has been undertaken in the field of conjugated polymers because of their possible industrial optoelectronic applications, such as light-emitting diodes (LEDs).¹ Soluble polyfluorenes are promising candidates for use as blue-light-emitting polymers in full-color organic displays because of their high thermal stability, high hole mobility, easy processability, and high quantum efficiencies. Various homopolyfluorenes and copolyfluorenes have been

prepared and used for the fabrication of blue LEDs.^{2–5} However, an undesired low-energy green band in the range of 500–600 nm is frequently generated in both the photoluminescence (PL) and electroluminescence (EL) of polyfluorenes during operation, and it limits the emission efficiency and damages the blue color purity and stability as well.^{2–6} Two opposite points of view on the origin of this green emission have been reported.^{7,8} According to the first, the green emission is attributable to the interchain aggregates and/or excimer formation of polyfluorenes.^{2(a),5(a),7} Consequently, dendronization,^{5(b),9} the introduction of spiro- or crosslinks,^{5(a,c),6(e)} substitution with bulky side groups,^{4(b–e),10} blending,^{5(d)} and the introduction of disorder units such as carba-

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zole,¹¹ pyridine,^{12–15} and thiophene¹⁶ have been applied to suppress intermolecular interaction. The second point of view states that the green-emission band is caused by keto defects of polyfluorenes, which are generated during the handling of the materials in air, or by a reaction with residual oxygen over the course of photophysical experimentation.⁸ Certain researchers have clarified the origin of the green-emission band as a fluorenone moiety and contradicted experimentally the assumption that intermolecular aggregates or excimers are involved.^{8,17} Wegner et al.¹⁸ prepared fluorene- and phenylene-based polymers with sulfonate side groups to prevent autoxidation and improve their spectral stability.

In this contribution, we describe the synthesis, characterization, photophysics, and EL of a new class of statistical copolyfluorenes that carry tetraphenylthiophene (TPT) units along the main chain. These copolyfluorenes were successfully prepared by a nickel-mediated Yamamoto coupling reaction between 2,7-dibromo-9,9-dihexylfluorene and 2,5-bis(4-bromophenyl)-3,4-diphenylthiophene. The latter was easily synthesized by a two-step synthetic procedure from inexpensive starting materials, namely, benzyl chloride and sulfur. TPT moieties have been introduced into the backbones of various polymers, such as polyimides,¹⁹ polyamides,²⁰ poly(amide imide)s,²¹ polyazomethines,²² and polymer precursors²³ (bismaleimides and bisnadimides). All these polymers have displayed outstanding solubility and thermal stability. Recently, light-emitting polymers containing TPT moieties have been reported.^{24–26} The introduction of thiophene units into the polyfluorene backbone is attractive because polythiophenes have superior stability in both neutral and doped states.²⁷ For thiophene-based polymers, one of the most striking features is the easy and wide electronic tunability by side-chain modification.²⁸

EXPERIMENTAL

Characterization Methods

IR spectra were recorded on a PerkinElmer 16PC Fourier transform infrared (FTIR) spectrometer with KBr pellets. ¹H NMR (400-MHz) spectra were obtained with a Bruker spectrometer. Chemical shifts (δ values) are given as parts per million with tetramethylsilane (TMS) as an internal standard. Ultraviolet–visible (UV–vis)

spectra were recorded on a Beckman DU-640 spectrometer with spectrograde tetrahydrofuran (THF). The PL spectra were obtained with a PerkinElmer LS45 luminescence spectrometer. The PL spectra were recorded with the corresponding excitation maximum as the excitation wavelength. Gel permeation chromatography (GPC) analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a Waters 2410 differential refractometer as a detector with polystyrene as the standard and THF as the eluent. Thermogravimetric analysis (TGA) was performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA, and weight-loss comparisons were made between comparable specimens. Dynamic TGA measurements were made at a heating rate of 20 °C/min in an atmosphere of N₂ or air at a flow rate of 60 cm³/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA instrument with a loaded penetration probe at a scanning rate of 10 °C/min in N₂ with a flow rate of 60 cm³/min. The TMA experiments were conducted at least in duplicate to ensure the accuracy of the results. The TMA specimens were pellets 10 mm in diameter and ~1 mm thick prepared by the pressing of a powder of the polymer for 3 min under 8 kp/cm² at the ambient temperature. The glass-transition temperature (T_g) was assigned by the first inflection point in the TMA curve, and it was obtained from the onset temperature of this transition during the second heating. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

To measure the PL quantum yield (Φ_f), a degassed solution of the polymer in THF was prepared. The concentration was adjusted so that the absorbance of the solution was lower than 0.1. The excitation was performed at the corresponding excitation maximum, and a solution, in 1 N H₂SO₄, of quinine sulfate, which has a Φ_f value of 0.546, was used as a standard.

Reagents and Solvents

2,7-Dibromofluorene was synthesized by a reported method.²⁹ 2,7-Dibromo-9,9-dihexylfluorene was synthesized by the reaction of 2,7-dibromofluorene with 1-bromohexane, which was catalyzed by concentrated NaOH (aqueous, 50% w/w), in the presence of the phase-transfer catalyst trimethylbenzylammonium chloride.³⁰ This monomer was purified by repeated recrystallizations

from ethanol. However, this monomer was not further purified³¹ by a treatment with potassium *tert*-butoxide to remove 9-monoalkylated fluorene derivatives that afforded keto defects. Dimethylformamide (DMF), toluene, and dichloromethane were dried by distillation over CaH₂. All other solvents and reagents were analytical-grade quality, were purchased commercially, and were used without further purification.

Preparation of the Monomers and Polymers

2,3,4,5-Tetraphenylthiophene (1)

Compound **1** was prepared according to a literature procedure.¹⁹

2,5-Bis(4-bromophenyl)-3,4-diphenylthiophene (2)

Compound **2** was prepared according to a literature procedure,³² which was modified as follows. A flask was charged with a solution of **1** (1.37 g, 3.53 mmol) in dichloromethane (20 mL). Bromine (1.13 g, 7.06 mmol), diluted with dichloromethane (15 mL), was added dropwise to the stirred solution. The mixture was subsequently stirred for 15 h at room temperature. Then, it was poured into methanol. The pale yellow precipitate was filtered, dried, and recrystallized from 1,2-dichloroethane to afford **2** (1.10 g, yield = 55%, mp = 250 °C, lit.³⁰ 250–252 °C).

IR (KBr, cm⁻¹): 1603, 1478, 1390, 1072, 1006, 822, 730, 696. ¹H NMR (CDCl₃, ppm): 7.35 (d, 4H, *J* = 8.4 Hz); 7.12 (m, 10H); 6.94 (d, 4H, *J* = 6.1 Hz). ¹³C NMR (CDCl₃, ppm): 140.0, 137.4, 135.9, 133.0, 131.5, 130.7, 130.6, 128.0, 126.9, 121.5. ELEM. ANAL. Calcd. for C₂₈H₁₈Br₂S: C, 61.56%; H, 3.32%. Found: C, 61.18%; H, 3.37%.

Polymerization

The preparation of copolymer PF-Th 5 is given as a typical example for the preparation of the PF-Th copolymers and the homopolymer PF. In a dry flask, 2,2-bipyridine (0.2865 g, 1.83 mmol) and bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)₂; 0.5045 g, 1.83 mmol] were added in a glovebox. After the flask was taken from the glovebox, 1,5-cyclooctadiene (0.1984 g, 1.83 mmol) and anhydrous DMF (10 mL) were injected under argon. The mixture was stirred at 80 °C for half an hour to obtain a dark blue catalyst solution. In another dry flask, 2,7-dibromo-9,9-dihexylfluorene (0.5747 g, 1.17 mmol) and compound **2** (0.0335 g, 0.06 mmol) were dissolved in toluene

(10 mL) under argon. The catalyst solution was slowly transferred to the monomer solution. The polymerization was maintained at 80 °C for 4 days under argon. After this time, 0.10 g of bromobenzene was added to the reaction mixture for end capping, and heating at 80 °C was continued for 1 day. After the reaction was finished, polymer PF-Th 5 was precipitated as a pale yellow solid from an equivalent volume mixture of concentrated HCl, methanol, and acetone. The isolated polymer was purified by precipitation from a THF solution into methanol (0.11 g, yield = 27%).

The polymers were characterized with FTIR and ¹H NMR spectroscopy as follows.

Homopolymer PF

IR (KBr, cm⁻¹): 3064, 2920, 2852, 1598, 1452, 1414, 1254, 1110, 1058, 1004, 876, 804, 750. ¹H NMR (CDCl₃, ppm): 7.51 (s, 2H); 7.44 (s, 4H); 1.91 (m, 4H); 1.11–0.78 (m, 16H); 0.57 (br, 6H).

Copolymer PF-Th 50

IR (KBr, cm⁻¹): 3064, 2944, 2920, 2852, 1598, 1568, 1538, 1446, 1414, 1392, 1370, 1254, 1178, 1106, 1066, 1004, 876, 804, 764, 730, 698, 662, 604, 506, 486. ¹H NMR (CDCl₃, ppm): 7.52 (s, 2H); 7.50 (s, 4H); 7.30 (s, 4H); 7.14–7.12 (m, 10H); 6.94–6.93 (m, 4H); 1.93–1.89 (m, 4H); 1.13–1.04 (m, 16H); 0.58 (br, 6H).

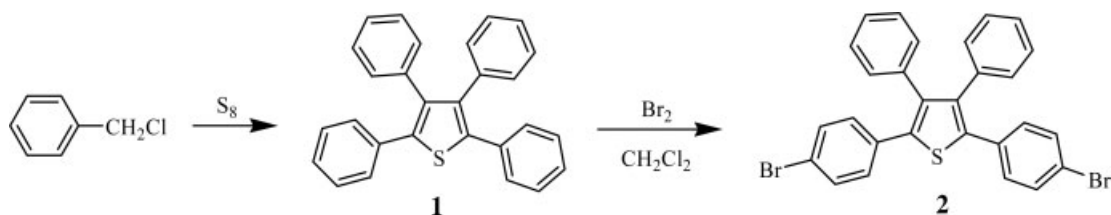
The other copolymers displayed FTIR and ¹H NMR spectra similar to those of PF-Th 50, except that the relative intensities of the signals were different because of the different compositions of the copolymers.

RESULTS AND DISCUSSION

Synthesis and Characterization

Scheme 1 outlines the synthesis procedure used to prepare key monomer **2**. In particular, **1** was prepared by the reaction of benzyl chloride with sulfur according to the literature.¹⁹ The latter was brominated with bromine in a molar ratio of 1:2 in dichloromethane to afford **2**.³² This monomer was fully characterized by elemental analysis and ¹H NMR and ¹³C NMR spectroscopy.

Homopolymer PF and the statistical PF-Th copolymers incorporating the TPT units were prepared via a nickel-mediated Yamamoto coupling reaction³³ by the simple variation of the relative ratios of 2,7-dibromo-9,9-dihexylfluorene and

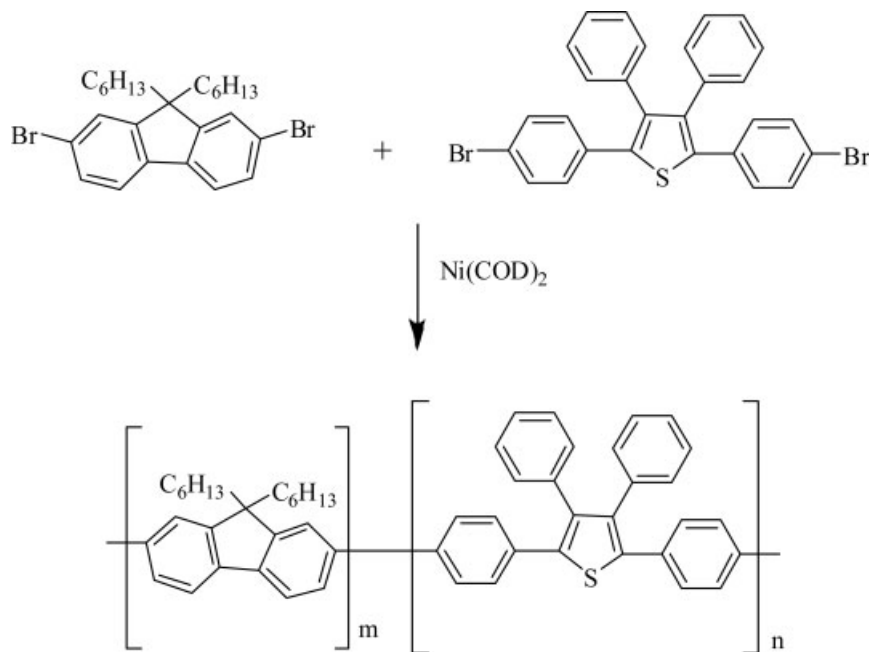


Scheme 1

comonomer **2** (Scheme 2). In this reaction, at first a solution of Ni(COD)_2 , 2,2'-bipyridine, and cyclooctadiene in DMF was heated at 80 °C for 0.5 h. A degassed solution of the two comonomers was then added, and heating was continued for 4 days to ensure polymerization. Finally, an excess of bromobenzene was added to the mixture for end capping and the removal of any residual bromine functionalities, which might act as fluorescence quenching sites. All polymers remained in solution during the polymerization process, and this led to the increase in their molecular weight. Homopolymer PF was synthesized under the same conditions for comparison. The number-average molecular weights (M_n 's) were determined

by GPC with polystyrene standards to be in the range of 8600–18,200 with a polydispersity index of 1.9–2.7 (Table 1).

The IR and ^1H NMR spectra of the polymers were consistent with their chemical structures. Representative FTIR and ^1H NMR spectra of homopolymer PF and copolymer PF-Th 50 are shown in Figures 1 and 2. Upon a comparison of their IR spectra, PF-Th 50 showed additional characteristic absorptions at 3046 (CH stretching), 1066 and 1004 (ring breathing), and 730 and 698 cm^{-1} (CH deformation) of the thiophene ring. These absorptions were also encountered at the same or slightly different frequencies in the IR spectrum of monomer **2**. The ^1H NMR spectrum



PF : $n/m = 0/100$

PF-Th 5: $n/m = 5/95$

PF-Th 20: $n/m = 20/80$

PF-Th 50: $n/m = 50/50$

Scheme 2

Table 1. Molecular Weights, T_g Values, and Photophysical Properties of the Polymers^a

Polymer	M_n^b	M_w/M_n^b	T_g (°C) ^c	$\lambda_{a,max}$ in a THF Solution (nm) ^d	$\lambda_{f,max}$ in a Solution (nm)	Φ_f in a Solution ^e	$\lambda_{a,max}$ in a Thin Film (nm) ^d	E_g (eV) ^f	$\lambda_{f,max}$ in a Thin Film (nm)	Φ_f in a Film ^g
PF	18,200	2.7	63	383	418, 439	0.57	383	2.89	424, 444, 518	1.00
PF-Th 5	16,500	2.5	78	383	419, 438	0.62	386	2.87	445, 521	1.83
PF-Th 20	13,100	2.6	142	381	440	0.61	389	2.85	448, 519	1.26
PF-Th 50	8,600	1.9	149	330	417, 439	0.32	331	3.28	419, 439	0.95

^a The italicized numerical values denote absolute maxima. The PL emission spectra were recorded at a 395 nm excitation wavelength.^b Determined by GPC with polystyrene standards.^c Determined by TMA with a penetration probe.^d From UV-vis spectra.^e With respect to quinine sulfate in 0.10 M H₂SO₄.^f Calculated from UV-vis spectra in thin films.^g Estimated by comparison with the fluorescence intensity of a PF thin film. A value of $\Phi_f = 1$ is given for PF, and the Φ_f values of the other polymers are given with respect to that of PF.

of PF-Th 50 clearly indicated the incorporation of TPT moieties into the polymer backbone because it displayed additional peaks at 7.34, 7.11, and 6.93 ppm, which are assigned to the aromatic protons of TPT labeled g, h, and f, respectively, in Figure 2. The resonances at 7.52 and 7.45 ppm are assigned to the aromatic protons labeled e and d, respectively, of the fluorene unit, whereas those in the region of 1.32–0.56 ppm are associated with the aliphatic protons labeled a, b, and c in the hexyl chains.

The thermal stability of the polymers was evaluated by TGA, and it gradually increased as the TPT fraction in the copolymers increased. The thermal decomposition temperature (at a 5% weight loss) of the polymers was above 350 °C in an atmosphere of N₂. The T_g values were determined³⁴ by the TMA method with a penetration probe (Table 1). They were recorded from the onset temperature of these transitions during the second heating (Fig. 3). T_g gradually increased with increasing TPT content in the copolymers. In particular, the T_g value steadily increased from 63 °C for PF to 149 °C for PF-Th 50. T_g values of 55³⁵ and 67 °C^{2(e),10} have been reported for PF.

Photophysical Properties

The photophysical properties of the polymers were investigated in dilute (10^{−5} M) THF solutions and in the solid state, and they are summarized in Table 1. The normalized absorption and PL emission spectra are shown in Figures 4 and 5, respectively. PF has an absorption maximum at 383 nm corresponding to the π – π^* transition of the polyfluorene backbone. The absorption spectra of PF-Th 5 and PF-Th 20 in solutions and in the solid state are almost identical to that of PF. This suggests that the TPT segments did not disrupt the π conjugation along the backbone even when their concentration in the copolymers was 20 mol %. The absorption spectra of these polymers in thin films were broader than those in solutions, probably because of the increased intermolecular interactions between neighboring molecules in the film state. It seems that for TPT concentrations lower than 20 mol %, the electronic properties of the copolymers were dominated by the fluorene moieties, and the TPT units did not really influence them. PF-Th 50 displayed a strongly blueshifted absorption spectrum with respect to the other polymers with a maximum ($\lambda_{a,max}$) at 330 nm in a solution and in a thin film. In particular, $\lambda_{a,max}$ of PF-Th 50 was blueshifted

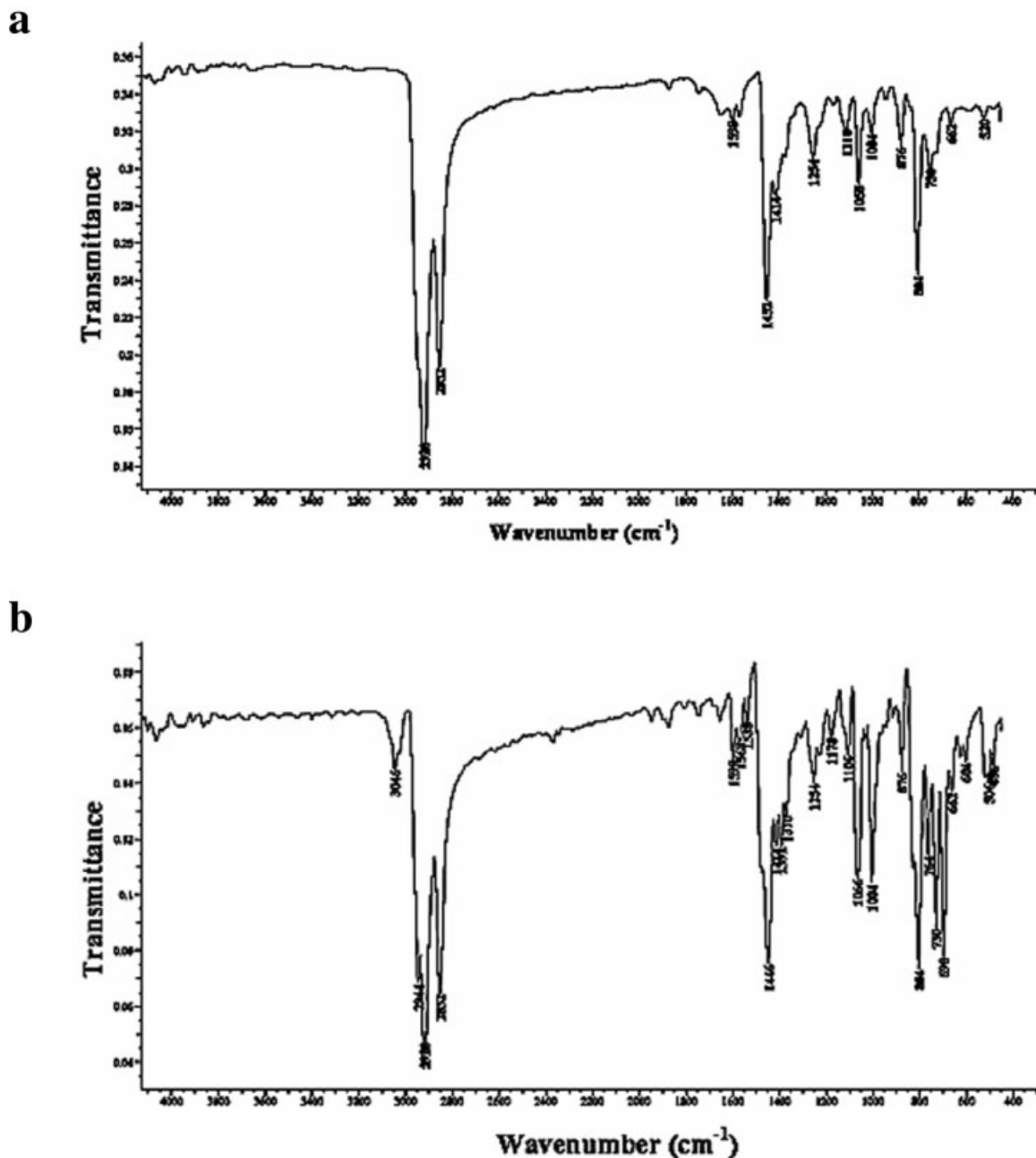


Figure 1. FTIR spectra of (a) homopolymer PF and (b) copolymer PF-Th 50.

by ~ 53 nm in comparison with that of the other polymers. This means that the π -electron delocalization of the polymer main chain was interrupted by TPT when its concentration in the copolymer was 50 mol %. Moreover, the absorption onset of the PF-Th 50 spectrum shifted to a higher energy in comparison with that of the other polymers, indicating a shortened conjugation length. The incorporation of such kinked structures into the polymer backbone has been used successfully in

poly(*p*-phenylenevinylene)s³⁶ and polyfluorenes³⁷ to shorten the conjugation length and tune the emission colors. The optical band gap (E_g) of the polymers calculated from the onset of the absorption spectra in thin films was 3.82 eV for PF-Th 50 and almost the same for the other polymers (2.85–2.89 eV).

The solutions of all polymers in THF emitted intense blue light with a PL maximum ($\lambda_{f,max}$) at 418–440 nm under excitation at 395 nm

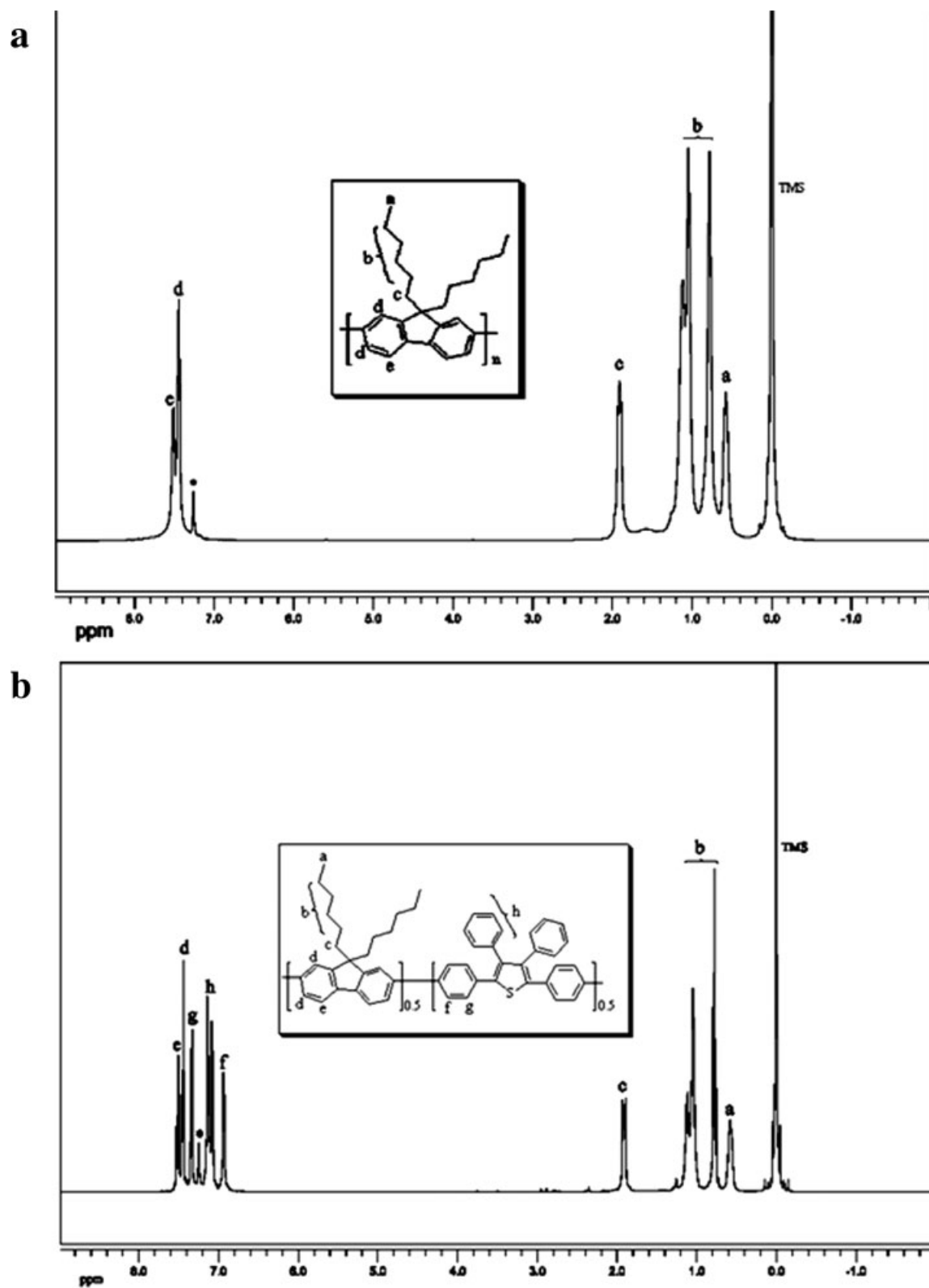


Figure 2. ^1H NMR spectra in CDCl_3 solutions of (a) homopolymer PF and (b) copolymer PF-Th 50. The peak of the solvent is marked with an asterisk.

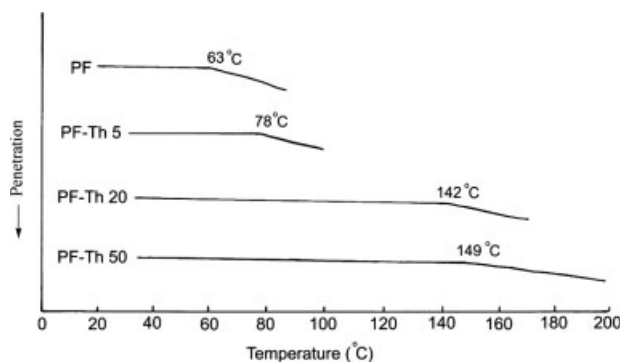


Figure 3. TMA traces of homopolymer PF and copolymers PF-Th (heating rate = 20 °C/min).

[Fig. 5(a)]. The PL emission spectrum of PF exhibited the typical vibronic progression with the 0–0 PL emission band at 418 nm and the 0–1 transition at 439 nm.^{6(a)} All the polymers, except PF-Th 20, showed the same pattern with $\lambda_{f,max}$ at 418 nm and a shoulder at 439 nm. In contrast, PF-Th 20 displayed a broad PL curve with $\lambda_{f,max}$ located at 440 nm.

The PL emission spectrum of the PF thin film [Fig. 5(b)] under excitation at 395 nm displayed $\lambda_{f,max}$ at 424 nm and a shoulder at 444 nm. In addition, it displayed a small shoulder at 518 nm that was assigned to traces of keto defects leading to fluorenone.⁸ Thin films of PF-Th 5 and PF-Th 20 emitted intense blue-green light with two well-resolved peaks at 445 and 520 nm. In the case of PF-Th 5, the two emission peaks are of about equal intensity, whereas for PF-Th 20, the dominant peak is that at 445 nm. The green band at 520 nm of these copolymers could be attributed to a combined effect of the keto defects and TPT units. Because the solutions of these copolymers emitted only blue light, the green band appeared in the solid state, in which strong chain interactions occurred. A further increase of the TPT fraction in the copolymer enhanced the blue emission of the copolymer thin films. Specifically, the PF-Th 50 thin film emitted pure blue light with $\lambda_{f,max}$ at 419 nm and a shoulder at 439 nm. The PL spectrum of this polymer was slightly (~ 5 nm) blue-shifted with respect to that of PF, and the green emission at 520 nm almost completely disappeared. In this case, the effective conjugation length was reduced because the kinked TPT units caused high disorder that disrupted the π conjugation along the polymer backbone. The absorption spectra of PF-Th 50 confirmed this behavior. Changes probably took place in the solid-state packing of this copolymer, leading to reduced

exciton mobility. Thiophene-*co*-fluorene polymers¹⁶ that contained kinked 3,4-linked thiophene and linear 2,7-linked 9,9-dihexylfluorene showed solid-state emission spectra with maxima at 410–424 nm that were in line with the emission of PF-Th 50. On the other hand, alternating conjugated copolymers composed of 9,9-dihexylfluorene and substituted bithiophene or thiophene moieties³⁸ emitted in the solid state blue-green light (458–520 nm) with E_g values of 2.49–2.76 eV. These E_g values are somewhat lower than those of PF-Th 5 and PF-Th 20. Finally, copolyfluorenes containing thiophene or bithiophene moieties along the main chain,³⁹ which were synthesized through the Stille coupling reaction, showed band gaps of 2.4 eV.

The Φ_f values of all the polymers in THF solutions were determined⁴⁰ with respect to quinine sulfate, and they are listed in Table 1. The highest Φ_f value of 0.62 was observed for PF-Th 5. Φ_f pro-

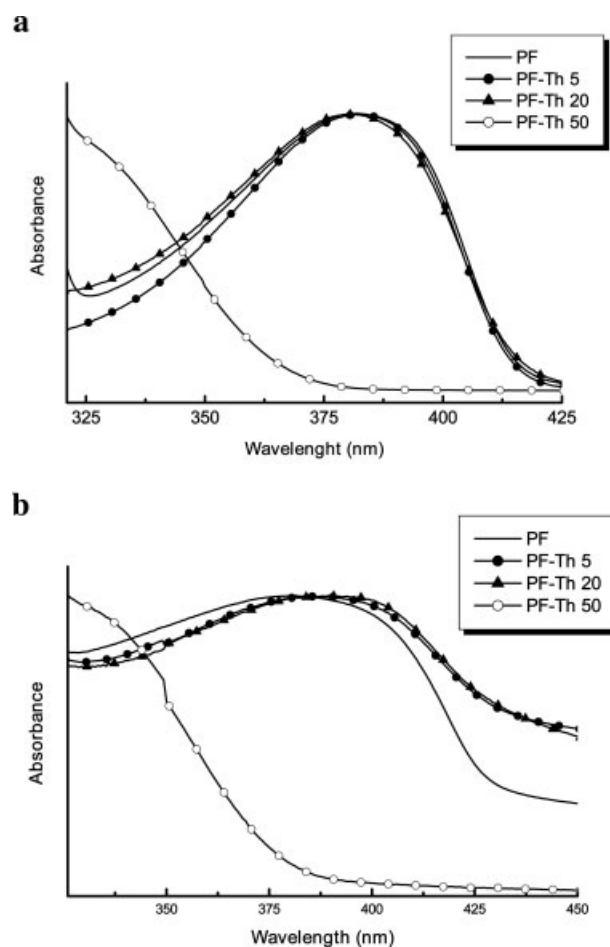


Figure 4. Normalized UV-vis absorption spectra of copolymers PF-Th and homopolymer PF in (a) THF solutions and (b) thin films.

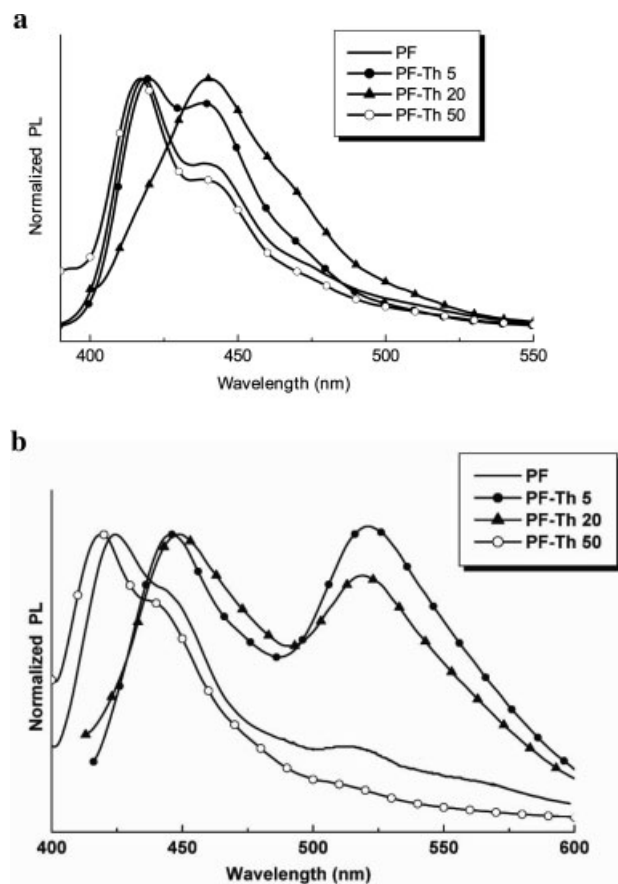


Figure 5. Normalized PL emission spectra of copolymers PF-Th and homopolymer PF in (a) THF solutions and (b) thin films.

gressively decreased with an increasing TPT fraction in the copolymers greater than 5 mol %. The lowest Φ_f value of 0.32 was obtained for PF-Th 50. In addition, solid-state Φ_f values were calculated by comparison with the fluorescence intensity of the PF thin film (Table 1). It seems that the Φ_f values of the polymer thin films followed a trend similar to that observed in solution. However, the relative fluorescence intensity of the PF-Th 50 thin film was slightly lower than that of PF and was reduced only by 5% versus 43% in solution.

EL Properties

The EL properties of a typical polymer, PF-Th 5, which exhibited the highest Φ_f value both in solution and in the solid state, and the reference homopolymer PF were investigated and compared. For this purpose, double-layer LEDs with the configuration indium tin oxide (ITO)/poly[3,4-(ethylenedioxy)thiophene] (PEDOT)/polymer/LiF/Al were fabricated and characterized.³⁷ The cor-

responding EL spectra, normalized with respect to the 0–0 emission band and shown in Figure 6, are similar to the thin-film PL spectra. The EL spectra of PF-Th 5, recorded under various bias voltages, had two main bands: one around 427 nm and the other at 528 nm. As mentioned previously, the band at 528 nm is assigned to the keto defects and the TPT units. It seems clear that the intensity of the green peak at 528 nm significantly increased with increasing bias voltage. At 6.0 or 8.0 V, the intensity of the green peak was slightly lower or higher, respectively, than that of the blue peak at 427 nm, and the EL curve was comparable to the thin-film PL curve. At 10.0 V, the green peak was ~3.5 times more intense than the blue peak. On the other hand, the intensity of

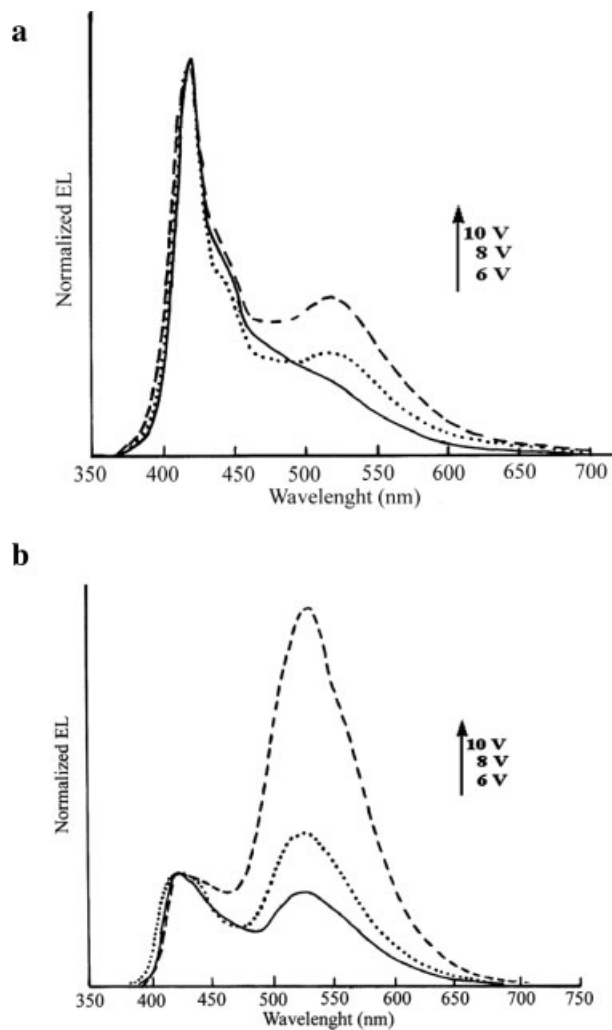


Figure 6. Normalized (with respect to the 0–0 emission band) EL spectra of LEDs of the ITO/PEDOT/polymer/LiF/Al type at various bias voltages of (a) homopolymer PF and (b) copolymer PF-Th 5.

the green peak at ~ 520 nm of the reference homopolymer PF, emerging only from keto defects,⁸ slightly increased with an increase in the bias voltage and remained much lower than that of the blue peak for all applied bias voltages. At 10.0 V, the green peak was ~ 2.5 times less intense than the blue peak. Thus, the introduction of the TPT segments into the polyfluorene backbone with a fraction of 5 mol % enhanced the green EL emission, especially at high bias voltages. A possible explanation is the variation in the charge recombination kinetics with the applied voltage. It seems that with increasing voltage, more charge recombination takes place on the fluorenone and TPT traps responsible for the green emission in comparison with the fluorene segments, which emit blue light. An analogous behavior has been reported recently for fluorenone-containing polyfluorenes.⁴¹

The current density/voltage and luminescence/voltage characteristics of the LEDs for PF and PF-Th 5 are shown in Figure 7(a,b), respectively. The turn-on voltages (the voltages at which the EL emissions were visible to the eye) for the two polymers were comparable at ~ 4.0 V. The PF homopolymer diode had a maximum brightness of 5 cd/m^2 at 9.2 V with a current density of 500 mA/cm^2 . On the other hand, the PF-Th 5 polymer diode had a maximum brightness of 43 cd/m^2 at 8.3 V with a current density of 360 mA/cm^2 . It seems that the introduction of the TPT units into the polyfluorene main chain with a fraction of 5 mol % improved the brightness of the LED.

Generally, the photophysical and EL properties of these polymers revealed the following features:

- Copolymer PF-Th 5 emitted intense blue-green light with a higher quantum yield both in a solution and in a thin film than the reference homopolymer PF and the other copolymers.
- The brightness of the LED made of copolymer PF-Th 5 was significantly higher than that of the reference homopolymer PF.
- No suppression of the green emission was achieved by the incorporation of TPT into the polyfluorene backbone up to 20 mol %.
- Copolymer PF-Th 50 emitted pure blue light even in the solid state, and it lacked almost completely the green band. However, its emission quantum yield was lower than that of homopolymer PF and the other copolymers.
- The color of the emitted light of the copolymer thin films could be changed between

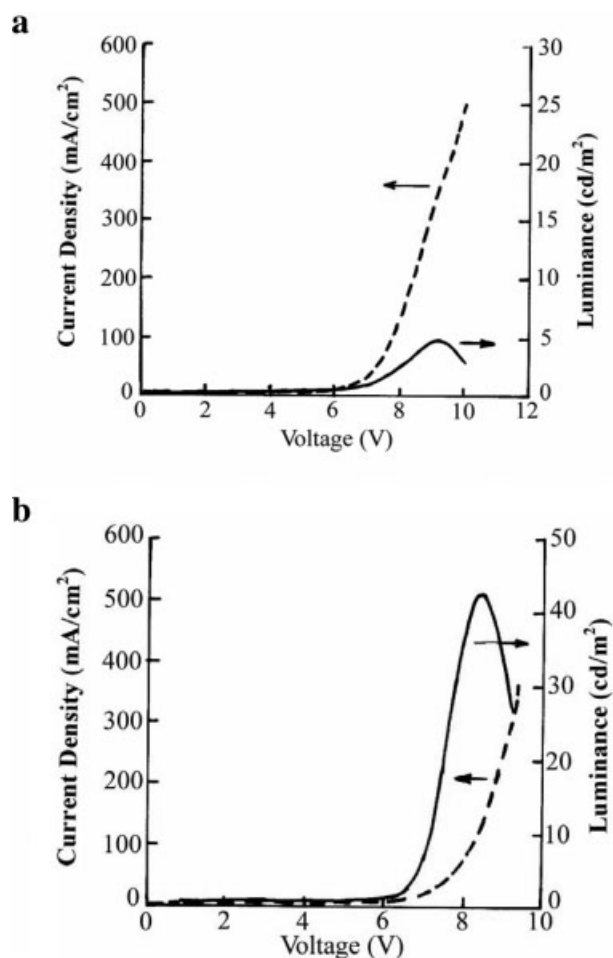


Figure 7. Current density/voltage/luminance characteristics of LEDs of the ITO/PEDOT/polymer/LiF/Al type from (a) homopolymer PF and (b) copolymer PF-Th 5.

blue and green, depending on the TPT concentration.

The preparation of other copolyfluorenes containing comonomers with various chemical structures to produce other emission colors and the fabrication of devices made of them are topics for future research.

CONCLUSIONS

A series of three soluble statistical copolymers of 9,9-dihexylfluorene and TPT were successfully synthesized via the nickel-mediated coupling reaction. The solutions of the polymers emitted blue light (418–440 nm). The emitted color of the

polymer thin films could be changed between blue and green (419–521 nm) by the variation of the TPT contents of the polymers. The polymer that contained 5 mol % TPT was the most luminescent, and its Φ_f values in a solution and in a thin film were 1.1 and 1.8 times higher, respectively, than those of the reference homopolymer PF. In addition, the LED of this polymer emitted blue-green light with a brightness ~ 8 times higher than that of PF. Finally, the copolymer with a TPT fraction of 50 mol % emitted pure blue light with a maximum at 419 nm.

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