Synthesis, Characterization, and Electroluminescence of Polyfluorene Copolymers Containing T-Shaped Isophorone Derivatives

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ABSTRACT: We have successfully synthesized a series of new fluorene-based copolymers, poly[(9,9-bis(4-octyloxy-phenyl)fluorene-2,7-diyl)-*co*-[2(3{2[4(2{4[bis(bromophenyl-4yl) amino]phenyl}vinyl)-2,5-bisoctyloxyphenyl]vinyl}-5,5-dimethyl-cyclohex-2-enylidene)malononitrile] (PFTBMs), with varying molar ratios of the low-energy band gap comonomer, 2(3{2[4(2{4[bis(4-bromophenyl)amino]phenyl}vinyl)-2,5-bisoctyloxyphenyl]vinyl}-5,5-dimethyl-cyclohex-2-enylidene)malononitrile (BTBM). To prepare BTBM (which has a T-shaped structure) from triphenylamine, dialkoxy phenyl, and isophorone, we introduced three individual segments of an isophorone derivative containing two cyanide groups at the carbonyl position, a dialkoxy phenyl group for increased solubility, and a triphenyl amine for effective charge transfer. Furthermore, we introduced vinyl linkages between each segment to increase the length of π-conjugation. The synthesized polyfluorene copolymers with the BTBM, PFTBMs, were synthesized via palladium-catalyzed Suzuki coupling reactions. The photoluminescence emission spectra of the synthesized polymers in solution did not show significant energy transfer from PBOPF segments to the BTBM units. Light-emitting devices based on these polymers were fabricated with an indium tin oxide/poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)/polymers/Balq/LiF/Al configuration. Examination of the electroluminescence emission of the synthesized polymers showed that the maximum wavelength shifted continuously toward long wavelengths with as the number of BTBM units in the polymer main chain was increased. In particular, a device using PFTBM 05 exhibited a maximum brightness of 510 cd/m^2 and a maximum current efficiency of 0.57 cd/A. © 2009 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 82–90, 2010

KEYWORDS: conducting polymers; conjugated polymers; fluorescence; isophorone; light-emitting diodes; polyfluorene

INTRODUCTION Over the past several years, conjugated polymers have attracted strong interest in scientific and technological fields because of their potential use as semiconductor and electroactive materials in a variety of applications, such as organic thin-film transistors,[1] organic bulk heterojunction photovoltaic cells,[2] nonlinear optical devices,[3] and organic polymer light-emitting diodes (PLEDs).[4] In particular, interest in PLED devices using conjugated polymers[5] has increased because such PLEDs have properties that are suitable for flat panel displays; easy processing from polymer solutions, low operating voltages compared with small molecules, faster response times than liquid crystal displays, and facile color tuning over the full visible range from blue to red via introduction of a diversity of comonomers.

Recently, studies of polyfluorenes and fluorene oligomers have explored the advantages of these materials over other conjugated polymers, yielding improved photoluminescence (PL) and electroluminescence efficiencies, thermal and electrical stabilities, and facilitating the introduction of diverse functional groups at the C-9 position of fluorene.[6,7] Furthermore, the properties of polyfluorene are easily modulated by introducing diverse low band gap comonomers because of its wide band gap of ~3.0 eV. This approach use methods widely used in color tuning, which involve the covalent attachment of a chromophore to the polymer. To date, the most widely used narrow energy band gap comonomers have been those containing aromatic heterocycles, such as thiophene, bithiophene, benzothiazole, and benzothidazoloe derivatives.[8,9] To enhance polyfluorene efficiencies, several studies have used strategies of blending, copolymerization, and end-capping with charge-transporting materials to achieve efficient charge injection.[10] We have reported that fluorene derivatives with bulky alkoxyphenyl substituents at the 9-position exhibit enhanced blue emission stability and

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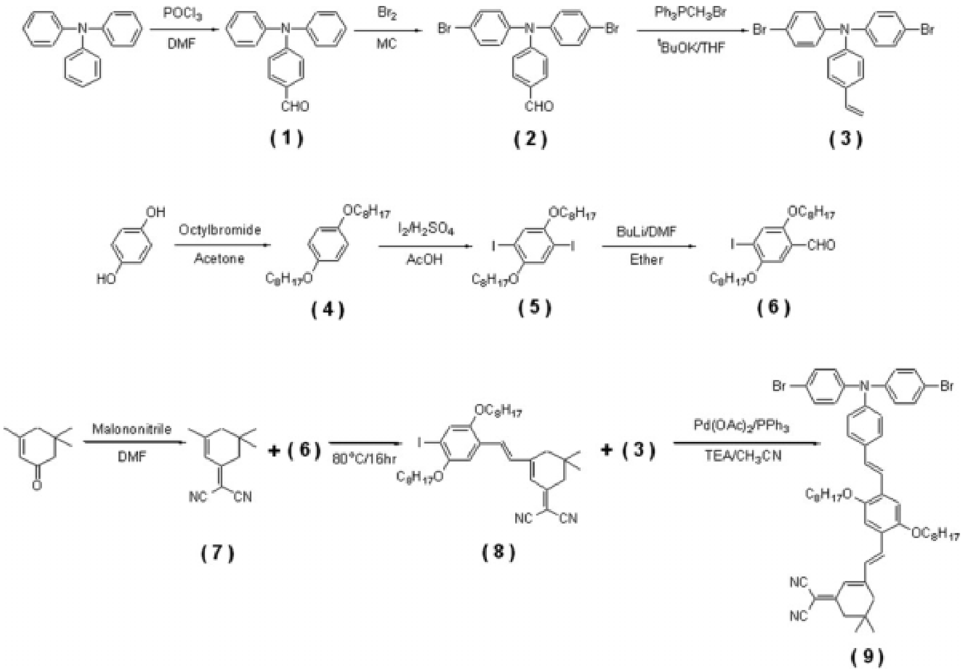


SCHEME 1 The synthetic routs of the BTBM.

superior device performance compared with alkyl-substituted polyfluorenes.[11]

Triarylamines, in amorphous glassy film states, show excellent hole mobilities at room temperature through time-of-flight measurements.[25] These materials have attracted considerable interest as hole-transport materials for use in multilayer organic electroluminescence (EL) devices[12,13] because of the low levels of their highest occupied molecular orbitals (HOMO) and high hole mobility. The former allows efficient hole injection from indium tin oxide (ITO) transparent anodes and reduces the likelihood of trapping.[14] Pernius et al.[15] reported the efficient blue-light emission EL properties of polyfluorenes containing a triphenyl amine derivative that enhanced hole-transporting abilities in the polymer chains.

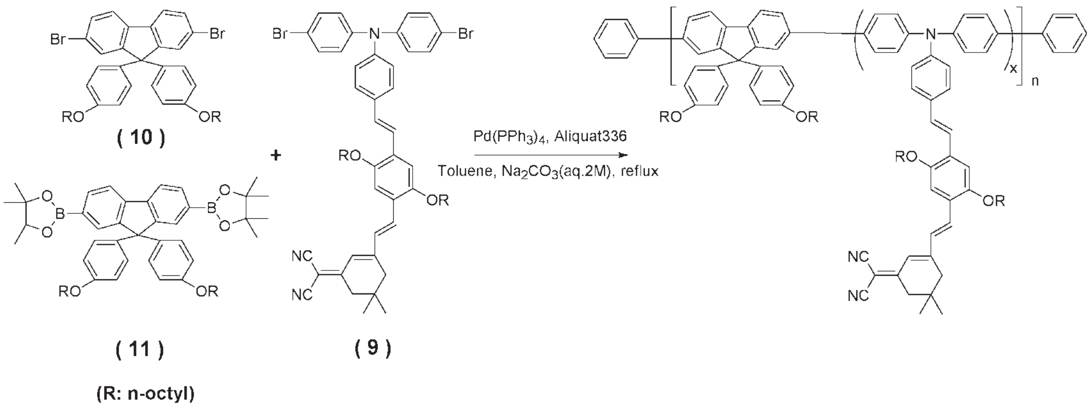
The well-known pyran-containing laser dyes, such as 4(dicyanomethylene)2-methyl-6[*p*(dimethylamino)styryl]4*H*-pyran (DCM) derivatives, have been widely used and are regarded as progressive red-emitting materials for OLED applications.[16] All DCM derivatives consist of two cyanide groups as the acceptor and a pyran ring as the donor, where the donor and acceptor are connected by a vinylene group. The architectures of these DCM derivatives yield a pure red color when combined with a suitable host material. They are usually synthesized by condensation reactions between aldehyde groups and dicyanomethylidenepyrans, which produce a doubly condensed product. A one-to-one stoichiometric ratio, however, tends to produce unwanted double-condensed products. These products are difficult to separate using chromatography or sublimation isolation.[17] The isophorone is not only similar in structure to DCM but also avoids forming the double-condensation byproduct because of its asymmetric structure. Lee and coworkers[17] and Ermer et al.[18] reported the efficient red-light emission EL properties of isophorone-based dopants.

In this article, we report the synthesis of polyfluorene copolymers containing isophorone derivatives, 2(3{2[4(2{4[bis(4-bromophenyl)amino]phenyl}vinyl)-2,5-bisoctyloxyphenyl]-vinyl}-5,5-dimethyl-cyclohex-2-enylidene)malononitrile (BTBM). BTBM contains a long conjugated system. It has three individual segments with an isophorone derivative containing two cyanide groups at the carbonyl position, a dialkoxy phenyl group for increased solubility, and a triphenyl amine for effective charge transfer. Furthermore, we introduced a vinyl linkage between each segment to increase the π-conjugation length. We systematically investigated the synthesis, thermal stability, optical properties, and electrical properties of the resulting polymers. The synthetic routes for the new PBOPF-based copolymers, PFTBMs, are given in Schemes 1 and 2.

EXPERIMENTAL

Measurements

NMR spectra were recorded using a Bruker AM 300 MHz spectrometer with tetramethylsilane as an internal reference. Elemental analysis was performed using an EA 1110 Fisons analyzer. UV–vis and PL spectra were recorded using Jasco V-530 and Spex Fluorolog-3 spectrofluorometers. Thermogravimetric analysis (TGA) was performed using a TA Q500 analyzer with a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetric measurements were made using TA Q100 instrument and operated under nitrogen atmosphere at a heating rate of 10 °C/min. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography



SCHEME 2 The synthetic routs of the copolymers, PFTBMs.

(GPC) on Viscotek T60A instrument, using tetrahydrofuran (THF) as eluent and polystyrene as standard. Cyclic voltammetry (CV) was performed on an AUTOLAB/PG-STAT12 model system with a three-electrode cell in a solution of Bu_4NBF_4 (0.10 M) in acetonitrile at a scan rate of 50 mV/s. A film of each polymer was coated onto a Pt wire electrode by dipping the electrode into a solution of the polymer. The measurements were calibrated using ferrocene as standard. LED devices were fabricated on glass substrates coated with ITO. The device configuration was ITO/PEDOT:PSS/polymer/Balq/LiF/Al structures. The procedure for cleaning the ITO surface included sonication and rinsing in deionized water, methanol, and acetone. The hole-transporting PEDOT:PSS layer was spin-coated onto each ITO anode from a solution purchased from Bayer. Each polymer solution in chlorobenzene was then spin-coated onto the PEDOT:PSS layer. The spin-casting yielded uniform polymer films with thicknesses of ~40 nm. A 40-nm-thick bis(2-methyl-8-quinolinolate)-4-(phenylphenolata)aluminum (Balq) electron-transporting layer was deposited, and a 1-nm-thick lithium fluoride layer and a 70-nm-thick aluminum layer were subsequently deposited at pressures below 10^{-6} Torr. EL spectra of the devices were obtained using a Minolta CS-1000. Current–voltage–luminance (*I-V-L*) characteristics were recorded simultaneously with the measurement of the EL intensity by attaching the photospectrometer to a Keithley 238 and a Minolta LS-100 as the luminance detector.

Materials

Triphenyl amine, malononitrile, isophorone, hydroquinone, 1-bromooctane, 2,7-dibromofluorenone, toluene (99.8%, anhydrous), *N,N*-dimethylformamide (99.8%, anhydrous), 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane, methyltriphenylphosphonium bromide, tetrakis-(triphenyl-phosphine)-palladium (0), palladium (II) acetate, triphenylphosphine, triethylamine, *N*-bromosuccinimide, and Aliquat®336 were purchased from Aldrich. All chemicals were used without further purification. 4-Diphenylamino-benzaldehyde (**1**), 4[bis(4-bromophenyl)amino] benzaldehyde (**2**), 1,4-bis-octyloxy-benzene (**4**), 2(3,5,5-trimethyl-cyclohex-2-enylidene)malononitrile (**7**), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)-fluorene (BOPF) (**10**), and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxy-phenyl)fluorene (**11**) were synthesized according to procedures outlined in the literature.[11,19,20] Solvents with analytical grade were used during the whole experiments, and all chemicals were used without further purification.

Synthesis of Bis(4-bromophenyl)-(4-vinylphenyl)amine (3)

4[Bis-(4-bromophenyl)amino]benzaldehyde (**2**) (3 g, 6.96 mmol) and methyltriphenylphosphonium bromide (7.45 g, 20 mmol) were dissolved in 10 mL of dry THF. Potassium *tert*-butoxide (50 mL, 1.0 M solution in THF) was added dropwise slowly to the resulting solution at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 for 12 h. The reaction mixture was poured into water and extracted with ethyl acetate. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to dryness under vacuum. The crude product was purified by column chromatography (petroleum ether/dichloromethane = 4:1) to give product (**3**) as a white solid. The resulting product yield was 80% (2.39 g).

^{1}H NMR ($CDCl_3$, ppm) 7.32–7.28 (m, 6H), 7.00 (d, 2H), 6.94–6.92 (m, 4H), 6.64–6.61 (m, 1H), 5.67–5.63 (d, 1H), 5.28–5.17 (d, 1H). ^{13}C NMR ($CDCl_3$, ppm) 146.38, 146.25, 135.92, 132.93, 132.34, 127.29, 125.51, 124.13, 115.64, 112.91. Anal. Calcd for $C_{20}H_{15}Br_2N$; C, 55.97; H, 3.52; N, 3.26. Found: C, 55.87; H, 3.61; N, 3.24.

Synthesis of 2,5-Diiodo-1,4-bis-octyloxy-benzene (5)

A solution of compound (**4**) (10 g, 30 mmol), KIO_3 (2.55 g, 12 mmol), and I_2 (8.35 g, 32.7 mmol) in acetic acid (100 mL)/conc. H_2SO_4 (1 mL)/H_2O (4 mL) was stirred at 80 °C for 24 h. After cooling, $Na_2S_2O_3$ aqueous solution was added until the purple color disappeared, then the mixture was poured into H_2O (250 mL) and extracted with dichloromethane. The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated to dryness under vacuum. Recrystallization from dichloromethane and hexane afforded product (**5**). The resulting product yield was 59% (10 g).

^{1}H NMR ($CDCl_3$, ppm) 7.14 (s, 2H), 3.89 (t, 4H), 1.76 (m, 4H), 1.53–1.28 (m, 20H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$, ppm) 152.84, 121.70, 85.67, 69.99, 32.01, 28.98, 28.01, 25.89, 22.14, 13.89. Anal. Calcd for $C_{22}H_{36}I_2O_2$; C, 45.07; H, 6.19. Found: C, 45.15; H, 6.23.

Synthesis of 4-Iodo-2,5-bis-octyloxy-benzaldehyde (6)

The obtained compound (**5**) (3.5 g, 5.97 mmol) was dissolved in diethyl ether (100 mL) at −78 °C. To a solution was added 3.75 mL (5.97 mmol) of butyllithium (1.6 M in hexane) by syringe. The mixture was stirred at −78 °C for 2 h. *N,N*-Dimethylformamide (0.66 mL, 8.96 mmol) was added to the solution, and the resulting mixture was stirred at −78 °C for 1 h, warmed to room temperature, and stirred for 40 h. The mixture was poured into water, extracted with dichloromethane, and dried over $MgSO_4$. The solvent was removed by solvent evaporation, and the residue was purified by column chromatography using ethylacetate/hexane (2/8, v/v) as the eluent. Recrystallization from dichloromethane and hexane afforded product (6). The resulting product yield was 85% (2.48 g).

^{1}H NMR ($CDCl_3$, ppm) 10.21 (s, 1H), 7.47 (s, 1H), 7.21 (s, 1H), 4.08 (t, 2H), 4.02 (t, 2H), 1.91 (m, 4H), 1.59–1.31 (m, 20H), 0.87 (t, 6H). ^{13}C NMR ($CDCl_3$, ppm) 189.02, 154.92, 152.02, 124.98, 124.58, 109.01, 96.65, 69.79, 69.22, 31.58, 28.92, 28.49, 28.38, 26.02, 25.99, 21.94, 13.80. Anal. Calcd for $C_{23}H_{37}I_2O_3$: C, 44.89; H, 6.06. Found: C, 45.02; H, 6.08.

Synthesis of 2{3[2(4-Iodo-2,5-bisoctyloxyphenyl)vinyl]-5,5-dimethyl-cyclohex-2-enylidene}malononitrile (8)

To a solution of compound (**6**) (5 g, 10.2 mmol) and compound (**7**) (2 g, 10.7 mmol) in 13 mL of *N,N*-dimethylformamide, 2.6 mL of acetic acid, 2.6 mL of piperidine, and 1.3 mL of acetic anhydride were added. The reaction mixture was heated at 80 °C for 8 h under stirring, cooled, and poured into water. After filtration, the crude reaction product was purified first by column chromatography onto silica gel using dichloromethane/ethyl acetate (4/1, v/v) as eluent. After evaporation of the solvent, the remaining reaction product was recrystallized from ethanol to obtain the pure product (**8**). The resulting product yield was 60% (3.98 g).

^{1}H NMR ($CDCl_3$, ppm) 7.32 (t, 2H), 6.95 (t, 2H), 6.82 (s, 1H), 4.00–3.92 (m, 4H), 2.56 (s, 2H), 2.43 (s, 2H), 1.84–1.77 (m, 4H), 1.37–1.27 (m, 16H), 0.87 (s, 6H), 0.87–0.84 (t, 6H). ^{13}C NMR ($CDCl_3$, ppm) 169.20, 154.23, 152.23, 151.76, 131.21, 129.34, 125.45, 123.89, 123.54, 113.47, 112.81, 109.14, 89.44, 70.06, 69.49, 42.90, 38.93, 31.96, 31.73, 31.71, 29.27, 29.26, 29.22, 29.16, 29.12, 27.94, 26.13, 26.02, 22.60, 22.58, 14.07, 14.05. Anal. Calcd for $C_{35}H_{49}IN_2O_2$: C, 64.02; H, 7.52; N, 4.27. Found: C, 64.15; H, 7.64; N, 4.15.

Synthesis of 2(3{2[4(2{4[Bis(4-bromophenyl) amino]phenyl}vinyl)-2,5-bisoctyloxyphenyl]vinyl}-5,5-dimethyl-cyclohex-2-enylidene)malononitril (9) (BTBM)

A solution of compound (**3**) (1 g, 2.33 mmol), compound (**8**) (1.6 g, 2.33 mmol), palladium (II) acetate (0.16 g, 0.24 mmol), triphenyphosphine (0.1 g, 0.38 mmol), and triethylamine (7 mL) in *N,N*-dimethylformamide (30 mL) was stirred at 130 °C for 24 h. The mixture was poured into water, extracted with dichloromethane, and dried over $MgSO_4$. The solvent was removed by solvent evaporation, and the residue was purified by column chromatography using dichloromethane/ethylacetate (4/1, v/v) as the eluent. Recrystallization from dichloromethane and methanol afforded product (**9**). The resulting product yield was 30% (0.6 g).

^{1}H NMR ($CDCl_3$, ppm) 7.43–7.33 (m 8H), 7.08–6.83 (m, 11H), 4.07–4.01 (m, 4H), 2.58 (s, 2H), 2.47 (s, 2H), 1.88–1.81 (m, 4H), 1.51–0.95 (m, 26H), 0.87–0.84 (m, 6H). Anal. Calcd for $C_{55}H_{63}Br_2N_3O_2$; C, 68.96; H, 6.63; N, 4.39. Found: C, 68.86; H, 6.54; N, 4.32. $m/z = 957.85$ (M^+).

General Polymerization Procedure

Into 100-mL two-neck flask was added dibromo compounds and diborolan compound in 25 mL of anhydrous toluene. Water-soluble Pd (0) complex, tetrakis-(triphenylphosphine)-palladiuim (1 mol %), was transferred into the mixture in a dry box. Subsequently, 2 M aqueous sodium carbonate deaerated for 30 min and the phase transfer catalyst, Aliquat®336 (several drops), in toluene purged under nitrogen for 1 h was transferred via cannula. The reaction mixture was stirred at 80 °C for 3 days, and then the excess amount of bromobenzene, the end-capper, dissolved in 1 mL of anhydrous toluene was added and stirring continued for 12 h. The reaction mixture is cooled to about 50 °C and added slowly to a vigorously stirred mixture of 200 mL of methanol. The polymer fibers are collected by filtration and reprecipitation from methanol and acetone. The polymers are purified further by washing for 2 days in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues, and column chromatography with a chloroform solution of the polymer. The reprecipitation procedure in chloroform/methanol is then repeated several times. The resulting polymers were soluble in common organic solvents. Yield: 50–68%.

PFTBM 05

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**11**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (0.995 equiv), and BTBM (**9**) (0.005 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–6.75 (∼33H), aliphatic; 3.90–3.85 (∼8H), 1.74–0.84 (∼70H). ELEM. ANAL. Found: C, 87.12; H, 9.04; N, 0.04.

PFTBM 1

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**11**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (0.99 equiv), and BTBM (**9**) (0.01 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–6.75 (∼33H), aliphatic; 3.90–3.85 (∼8H), 1.74–0.84 (∼70H). ELEM. ANAL. Found: C, 86.04; H, 8.90; N, 0.14.

PFTBM 5

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**11**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (0.95 equiv), and BTBM (**9**) (0.05 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–6.75 (∼33H), aliphatic; 3.90–3.85 (∼8H), 1.74–0.84 (∼70H). Elem. Anal. Found: C, 84.62; H, 8.41; N, 0.62.

PFTBM 10

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**11**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (0.90 equiv), and BTBM (**9**) (0.10 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–6.75 (∼33H), aliphatic; 3.90–3.85 (∼8H), 1.74–0.84 (∼70H). Elem. Anal. Found: C, 83.88; H, 8.33; N, 0.74.

PFTBM 25

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**11**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (0.75 equiv), and BTBM (**9**) (0.25 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–6.75 (∼33H), aliphatic; 3.90–3.85 (∼8H), 1.74–0.84 (∼70H). Elem. Anal. Found: C, 82.68; H, 8.21; N, 0.88.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polymers

The synthetic routes and structures of the polymers are shown in Scheme 2. A series of conjugated copolymers were synthesized via palladium-catalyzed Suzuki coupling reactions.[16,21] All PFTBMs were end-capped with bromobenzene. The actual compositions of the polymers were determined by elemental analysis.[16,21] The feed ratios of BTBM were 0.5, 1, 5, 10, and 25 mol % of the total amount of monomer, and the resulting ratios of BTBM units in the PFTBMs were 0.49, 1.96, 8.8, 10.69, and 12.77%, respectively. The actual ratios of PFTBM in the copolymers are similar to the feed monomer ratios in the first four cases. The lower than expected BTBM content for the feed ratio of 25 mol % is tentatively attributed to reduced reactivity of the bulky BTBM units during polymerization.[21] All copolymers were found to be soluble in common organic solvents such as THF, chloroform, and toluene, with no evidence of gel formation. Each copolymer was spin-coated onto a quartz plate coated with an ITO substrate and found to produce transparent and homogeneous thin films. The number-averaged molecular weights (M_n) of the copolymers, as determined by GPC using a polystyrene standard, were found to range from 19,300 to 22,800 with polydispersity indices ranging from 2.1 to 2.9. The yields of the copolymers ranged from 50 to 68%. The thermal transitions of the polymers were studied using differential scanning calorimetry under a nitrogen atmosphere. The thermograms for PFTBMs each contained only a glass transition around 86 °C, without features characteristic of the melting of liquid-crystalline phases. The thermal properties of the polymers were determined using TGA. All polymers were found to exhibit good thermal stability, losing less than 5% of their weight upon heating from 320 to 450 °C in TGA under a nitrogen atmosphere. Interestingly, PFTBM 10 and PFTBM 25 began decomposing at a lower temperature than the other polymers. We assume that this result originated from the BTBM units in the polymer main chain, because BTBM units have a low decomposition temperature due to their two vinyl linkages. Additionally, we found that the amount of weight loss at the start of thermal decomposition increased with increasing content of BTBM units in the polymer main chain. The TGA traces of the PFTBMs are shown in Figure 1. The polymerization results of the synthesized copolymers are summarized in Table 1.

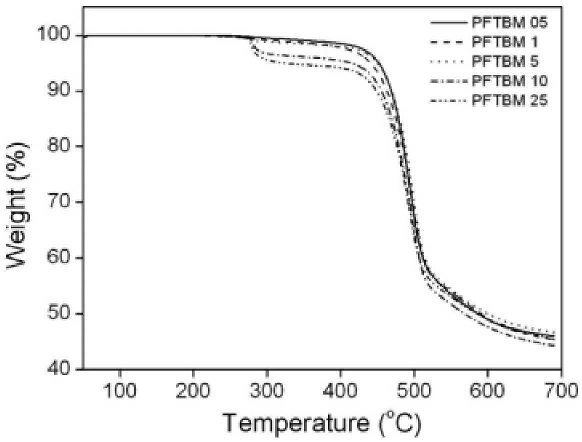


FIGURE 1 TGA traces of the synthesized PFTBM polymers.

Optical, Photoluminescence, and Electrochemical Properties

The UV–vis absorption spectra of the PFTBMs exhibit absorption maxima at 386 nm. Previous reports gave the UV–vis absorption maxima of PBOPF homopolymers at 391 nm in the film state.[11] Compared with these results, the UV–vis absorption maxima of the PFTBMs are at lower wavelengths than those of the PBOPF homopolymer[11] by ∼5 nm. We assume that this effect is due to the linkage between the nitrogen and phenyl groups in the diphenyl amine of the polymer main chain. The diphenyl amine units in the main chain disturb the conjugation of the polymer main chain because the nonconjugated structure shortens the conjugation length of the molecules, yielding a blue-shift in the absorption spectrum.[22] The absorptions at the spectral edge, around 425 nm, however, increased slightly with increasing content of BTBM units in the polymer main chain. These results indicate that the BTBM units are not involved in the polymer main-chain processes in the solution state. The normalized UV–vis absorption spectra of the polymers are shown in Figure 2(a). The normalized PL emission spectra are shown in Figure 2(b,c). In the solution phase [Fig. 2(b)], the PL spectra of all polymers exhibit emission maxima at 417 nm. The shapes of the PL emission spectra of the PFTBMs are similar to those of PBOPF homopolymers. Interestingly, the intensities of PL emission of the PFTBMs at 438 and 467 nm are slightly reduced, but the intensities at 553 nm are slightly elevated compared with the PBOPF PL emission spectrum. The PL spectra for thin films of the polymers [Fig. 2(c)], however, are quite different from the solution spectra. The PBOPF homopolymer film has a maximum PL emission in the blue region of the spectrum at 424 nm.[11]

TABLE 1 Physical Properties of the Synthesized PFTBM Polymers

Polymer	M_n[a]	PDI[a]	T_g (°C)	T_d (°C)[b]	Ratio (BTBM mol %) In the Feed Composition	 In the Copolymers[c]
PFTBM 05	21,200	2.3	86.1	450	0.5	0.49
PFTBM 1	19,700	2.1	86.5	450	1	1.96
PFTBM 5	21,300	2.8	84.5	440	5	8.8
PFTBM 10	22,800	2.7	83.2	412	10	10.69
PFTBM 25	19,300	2.9	80.2	320	25	12.77

[a] M_n and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

[b] Temperature resulting in 5% weight loss based on initial weight.

[c] Calculated by elemental analysis through calculation of the amount of nitrogen contained in copolymers.

Interestingly, the two strong and sharp PL peaks in the blue region of the spectrum of PBOPF are much weaker in intensity in the PL spectra of the copolymers. The PL maximum of the copolymer containing only 1% BTBM, PFTBM 1, is at 494 nm, which constitutes a large shift with respect to the PL maximum of PBOPF. As the BTBM content of the copolymers is increased, the intensities of the blue PL emission bands in the blue decrease. These large shifts in PL emission are probably due to intermolecular energy transfer,[23,26–27] from the BOPF group to the low band gap BTBM, which results in emission occurred mainly. The maxima of PL emission spectra are also slightly shifted to longer wavelengths because of increased BTBM content in the polymer main chain. This red shift in the PL emission spectrum may be due to the increased effective BTBM content in the copolymers. We assume that the differences in the solution and film state PL spectra for PFTBMs arise from the BTBM planarity, which allows more effective interchain interaction. To explain these results, we plan to investigate the polymer conformations and the influence of conformation on spectral properties. The optical properties of the synthesized polymers are summarized in Table 2.

To investigate the energy levels of their HOMOs and lowest unoccupied molecular orbitals, the electrochemical properties of PFTBMs were investigated by CV. A platinum electrode was coated with the polymers and used as the working electrode. The counter electrode was a platinum wire, and the reference electrode was an Ag/AgNO$_3$ (0.01 M) electrode. The electrochemical properties of the copolymers were investigated in an electrolyte consisting of a solution of 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile at room temperature under nitrogen at a scan rate of 50 mV/s. The measurements were calibrated using ferrocene as the standard.[24] Figure 3 shows the oxidation waves and energy levels of the copolymers as a result of the *p*-type doping. As shown in Figure 3, in the anodic scan and energy diagram, the onset of oxidation of PFTBMs was found to occur between 1.08 and 1.11 V, corresponding to ionization potentials of 5.75 and 5.78 eV, respectively. The onset of oxidation of BTBM was found to occur at 0.51 V, corresponding to

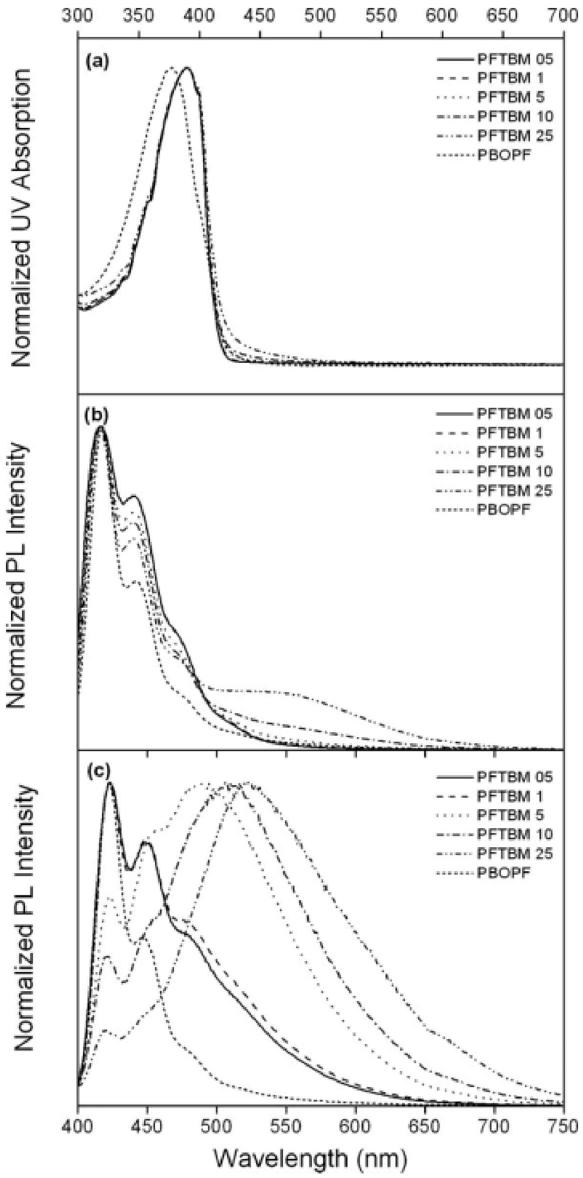


FIGURE 2 UV–vis absorption (a) and PL emission (b, solution) and (c, film) spectra of the synthesized polymers.

TABLE 2 Summary of the Optical Properties and Energy Levels of the Synthesized PFTBM Polymers

	Film, λ_{max} (nm)[a]				
Polymer	Absorption	Emission	$E_{onset,ox}$ (V)	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[c]
PFTBM 05	386	424	1.11	5.78	2.81
PFTBM 1	386	424	1.11	5.78	2.81
PFTBM 5	386	494	1.09	5.76	2.81
PFTBM 10	386	506	1.09	5.76	2.82
PFTBM 25	386	523	1.08	5.75	2.83
BTBM	–	–	0.51	5.18	3.10

[a] Measured as thin films on fused quartz plate.

[b] Determined from the onset voltage of the first oxidation potential with reference to ferrocene at 4.8 eV.

[c] Calculated from HOMO and energy of band gap (E_g) (E_g from UV–vis absorption edge).

ionization potentials of 5.18 eV. The results of CV studies of PFTBMs show that the onset of oxidation of PFTBMs was slightly shifted toward high HOMO levels by an increase in BTBM content in the polymer main chain. Unfortunately, a reduction wave was scarcely obtained. The onsets of oxidation and the energies of the HOMO levels of the PFTBMs are listed in Table 2.

Electroluminescence Properties and Current–Voltage–Luminance Characteristics

To investigate the electrical properties and performances of the copolymers in real devices, polymer EL devices with the configuration ITO/PEDOT:PSS (40 nm)/polymer (40 nm)/Balq (40 nm)/LiF (1 nm)/Al (70 nm) were fabricated. The EL spectra of the synthesized polymers are similar to their corresponding PL spectra, as shown in Figure 4. The EL emission in the blue region shifts to longer wavelengths as a function of increasing BTBM content in the polymer main chain. We presume that the EL emission properties can be explained by energy transfer from the higher energy state of the BOPF segments to the lower energy state of the BTBM units.[24] Such results are common for organic host-guest systems, in which the low-energy state unit acts as charge-trapping sites.[23] The maximum EL emission shifts increasingly to the red as the fraction of BTBM units increases. In particular, the EL emission around 650 nm increased with increasing BTBM content in the polymer main chain. This was not observed, however, for polymers with low BTBM content in the polymer main chain, PFTBM 05 and PFTBM 1. We presume that the main emission process effectively occurs in the polymer main chain between the BOPF segment and the TPA part of the BTBM unit. Interestingly, the red emission around 650 nm increased with increasing BTBM content in the polymer main chain. We presume that these results were caused by the isophorone moiety of the BTBM unit. We mentioned earlier that copolymers with low BTBM contents processed through polymer main chain. The BTBM unit has a T-shaped structure, and isophorone was introduced as part of the red-emitting material in the BTBM. The isophorone moiety of the BTBM unit participated in the electroluminescent process with increasing BTBM content in the polymer main chain. These results can be explained by the interchain interactions between BTBM units and other polymer chain. The polymer chromaticity values continuously shifted to the red, ($x = 0.21$, $y = 0.26$) to ($x = 0.30$, $y = 0.43$). The CIE coordinates of PFTBMs are shown in Figure 5. The voltage–luminance (*V-L*) and voltage–current efficiency characteristics of the devices are shown in Figure 6, and their performances are summarized in Table 3. The turn-on voltages of the PFTBM devices range from 5.4 to 12.4 V, yielding maximum brightness values in the range 140–720 cd/m^2. The *V-L* and voltage–current efficiency curves shift to slightly higher voltages when the number of BTBM units in the copolymers is increased. PBOPF[11] and the copolymers have similar band gaps and HOMO levels, so very similar electron and hole injection arise from the electrodes. Therefore, we assumed that the dramatic improvement on turn-on voltage achieved using the copolymers arise from the BTBM units in

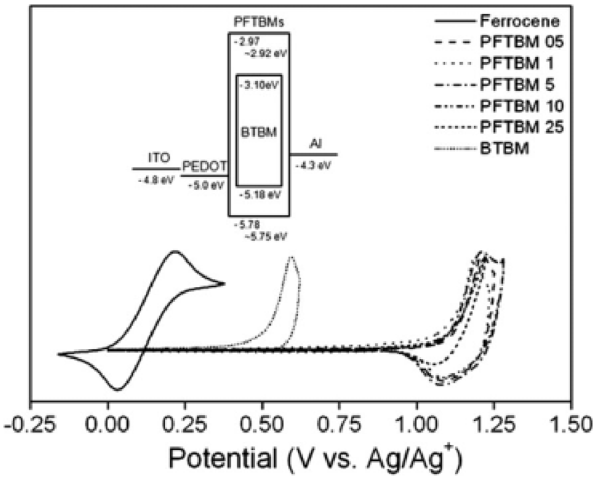


FIGURE 3 Cyclic voltammograms of the synthesized polymers and BTBM (inset: the proposed energy levels of BTBM and PFTBM).

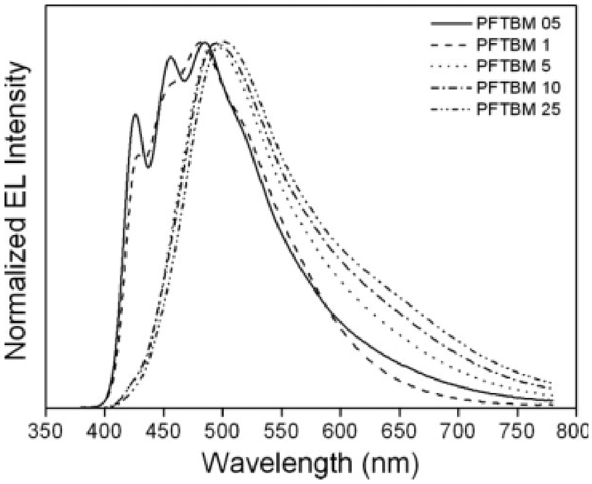


FIGURE 4 Electroluminescence spectra of PFTBM devices with ITO/PEDOT:PSS/polymer/Balq/LiF/Al configurations.

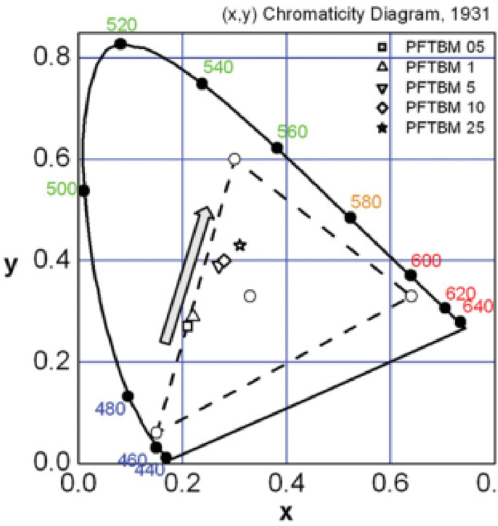


FIGURE 5 CIE coordinates (x,y) of PFTBMs (NTSC-dashed line).

the copolymer, which produce strong charge-trapping sites, resulting in the higher turn-on voltages measured in the PFTBM devices.[24] The PFTBM 05 device has the best performance, with a maximum brightness of 510 cd/m^2 at 10 V and a maximum current efficiency of 0.57 cd/A at 7 V. We suggest that PFTBM 05 produces balanced electron and hole injection in the device and that the energy transfer is efficient between the blue-light–emitting BOPF segments and the orange-light–emitting BTBM units. Although the BTBM was shown low color tunability in the polymer main chain because of competitive process between polymer main chain and intermolecular interaction, we believe that these electroluminescence characteristics could be further improved in future work by optimizing the film morphology, layer thickness, and postproduction treatment conditions.

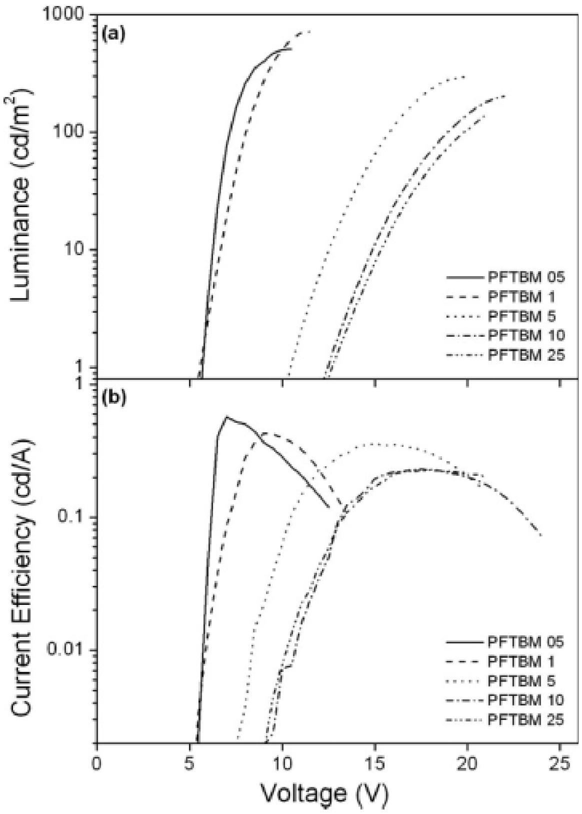


FIGURE 6 Voltage–luminance (V-L) (a) and voltage–current efficiency (b) characteristics of the synthesized PFTBM polymers.

CONCLUSIONS

We have successfully synthesized a series of new fluorene-based copolymers (PFTBMs) with varying molar ratios of the low-energy band gap comonomer, BTBM. To prepare a low-energy gap comonomer, we used an isophorone derivative containing a long conjugated system. The isophorone derivative has three individual segments containing cyanide groups at the carbonyl position, a dialkoxy phenyl group for increasing solubility, and a triphenyl amine for effective charge transfer. Furthermore, we introduced a vinyl linkage between each segment to increase the π-conjugation length. The PFTBMs were synthesized via palladium-catalyzed Suzuki coupling reactions. These polymers glass transition temperatures were similar to the PBOPF homopolymer and were found to be thermally stable and readily soluble in common organic solvents. The UV–vis absorption and PL emission spectra of the synthesized polymers did not show significant energy transfer from PBOPF segments to the BTBM units in solution. PL in film and EL emissions, however, were indicated that maximum spectra were shifted slightly to red due to interchain interactions between BTBM units and other polymer chain. The onset of oxidation of the PFTBMs was shifted slightly to higher HOMO levels by an increase in BTBM content in the polymer main chain. The PFTBM 05

TABLE 3 Summary of the EL Device Performances of the Synthesized PFTBM Polymers

Polymer	λ_{max} (nm)	Luminance$_{max}$ (cd/m^2)	Current Efficiency (cd/A)	EQE (%)	CIE Coordinates (x, y)[a]
PFTBM 05	426, 456, 480	510	0.57	0.3	(0.21, 0.26)
PFTBM 1	485	720	0.43	0.23	(0.21, 0.29)
PFTBM 5	492	300	0.36	0.17	(0.27, 0.39)
PFTBM 10	495	200	0.23	0.11	(0.28, 0.40)
PFTBM 25	501	140	0.23	0.11	(0.30, 0.43)

[a] Determined from EL spectra (Fig. 4).

device showed the best performance, with a maximum brightness of 510 cd/m^2 at 10 V and a maximum current efficiency of 0.57 cd/A at 7 V. We suggest that PFTBM 05 produces balanced electron and hole injection in the device, and that energy transfer is efficient between the blue-light–emitting BOPF segments and the orange-light–emitting BTBM units.

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REFERENCES AND NOTES

1 Sirringhaus, H.; Tessler, N.; Friend, R. H. Science 1998, 280, 1741–1744.

2 Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. Nature 1995, 376, 498–500.

3 Prasad, P. N.; Williams, D. J. Introduction to Nonlinear Effects in Monomers and Polymers; Wiley: New York, 1991.

4 (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. Nature (London) 1990, 347, 539–541; (b) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. Nature (London) 1992, 357, 477–479.

5 (a) Grimsdale, A. C.; Chan, K. L.; Martin, R. E.; Jokisz, P. G.; Holmes, A. B. Chem Rev 2009, 109, 897–1091; (b) Jeong, E.; Kim, S. H.; Jung, I. H.; Xia, Y.; Lee, K.; Suh, H.; Shim, H.-K.; Woo, H. Y. J Polym Sci Part A: Polym Chem 2009, 47, 3467–3479.

6 (a) Fukuda, M.; Sawada, K.; Yoshino, K. Jpn J Appl Phys 1989, 28, 1433–1435; (b) Pei, Q.; Yang, Y. J Am Chem Soc 1996, 118, 7416–7417; (c) Leclerc, M. J Polym Sci Part A: Polym Chem 2001, 39, 2867–2873; (d) Cho, H. J.; Hwang, D. H.; Lee, J. D.; Cho, N. S.; Lee, S. K.; Lee, J.; Jung, Y. K.; Shim, H. K. J Polym Sci Part A: Polym Chem 2008, 46, 797–802.

7 (a) Tsai, L. R.; Li, C. W.; Chen, Y. J Polym Sci Part A: Polym Chem 2008, 46, 5945–5958; (b) Scherf, U.; List, E. J. W. Adv Mater 2002, 14, 477–487; (c) Bonifácio, V. D. B.; Morgado, J.; Scherf, U. J Polym Sci Part A: Polym Chem 2008, 46, 2878–2883.

8 (a) Yang, J.; Jiang, C.; Zhang, Y.; Yang, R.; Yang, W.; Hou, Q.; Cao, Y. Macromolecules 2004, 37, 1211–1218; (b) Alam, M. M.; Tonzola, C. J.; Jenekhe, S. A. Macromolecules 2003, 36, 6557–6587; (c) Shen, Z.; Strauss, J.; Daub, J. Chem Commun 2002, 460–461; (d) Sun, D.; Rosokha, S. V.; Kochi, J. K. J Am Chem Soc 2004, 126, 1388–1401; (e) Lai, R. Y.; Fabrizio, E. F.; Lu, L.; Jenekhe, S. A.; Bard, A. J Am Chem Soc 2001, 123, 9112–9118; (f) Hsieh, B.-Y.; Chen, Y. J Polym Sci Part A: Polym Chem 2009, 47, 833–844.

9 (a) Hou, Q.; Zhou, Q.; Zhang, Y.; Yang, W.; Yang, R.; Cao, Y. Macromolecules 2004, 37, 6299–6305; (b) Cho, N. S.; Hwang, D.-H.; Jung, B.-J.; Lim, E.; Lee, J.; Shim, H.-K. Macromolecules 2004, 37, 5265–5273; (c) Yeh, H.-C.; Chan, L.-H.; Wu, W.-C.; Chen, C.-T. J Mater Chem 2004, 14, 1293–1298; (d) Yeh, H.-C.; Yeh, S.-J.; Chen, C.-T. Chem Commun 2003, 2632–2633; (e) Yen, W.-C.; Pal, B.; Yang, J.-S.; Hung, Y.-C.; Lin, S.-T.; Chao, C.-Y.; Su, W.-F. J Polym Sci Part A: Polym Chem 2009, 47, 5044–5056.

10 (a) Herguth, P.; Jiang, X.; Liu, M. S.; Jen, A. K.-Y. Macromolecules 2002, 35, 6094–6100; (b) Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Müllen, K. Adv Mater 2002, 14, 809–811; (c) Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Müller, C. D.; Meerholz, K.; Yasuda, A.; Neher, D. Adv Mater 2001, 13, 565–570; (d) Grisorio, R.; Piliego, C.; Cosma, P.; Fini, P.; Mastrorilli, P.; Gigli, G.; Suranna, G. P.; Nobile, C. F. J Polym Sci Part A: Polym Chem 2009, 47, 2093–2104.

11 Lee, J.-H.; Hwang, D.-H. Chem Commun 2003, 2836–2837.

12 (a) Tang, C. W. Appl Phys Lett 1986, 48, 183–185; (b) Okutsu, S.; Onikubo, T.; Tamano, M.; Enokida, T. IEEE Trans Electron Devices 1997, 44, 1302.

13 Giebeler, C.; Antoniadis, H.; Bradley, D. D. C.; Shirota, Y. Appl Phys Lett 1998, 72, 2448–2450.

14 Redecker, M.; Bradley, D. D. C.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. Adv Mater 1999, 11, 241–246.

15 (a) Pernius, M.; Inbasekaran, M.; Woo, E. P.; Wu, W.; Wujkowski, L. Proc SPIE 1999, 93, 36221; (b) Hsieh, B.-Y.; Chen, Y. J Polym Sci Part A: Polym Chem 2009, 47, 1553–1566.

16 Tang, C. W.; Van Slyke, S. A.; Chen, C. H. J Appl Phys 1989, 65, 3610–3616.

17 Li, J.; Liu, D.; Hong, Z.; Tong, S.; Wang, P.; Ma, C.; Lengyel, O.; Lee, C.-S.; Kwong, H.-L.; Lee, S. Chem Mater 2003, 15, 1486–1490.

18 Ermer, S.; Lovejoy, S. M.; Leung, D. S.; Warren, H. Chem Mater 1997, 9, 1437–1442.

19 (a) Ahn, T.; Song, S.-Y.; Shim, H.-K. Macromolecules 2000, 33, 6764–6771; (b) Park, M.-J.; Lee, J.-H.; Hwang, D.-H. Curr Appl Phys 2006, 6, 752–755.

20 Ichiki, K.; Consta, S. J Phys Chem B 2006, 39, 19176–19182.

21 Chen, C. H.; Shi, J.; Tang, C. W. Macromol Symp 1997, 125, 1.

22 Lee, R.-H.; Wang, Y.-Y. J Appl Polym Sci 2008, 107, 3459–3468.

23 Chuang, C.-Y.; Shih, P.; Chien, C.-H.; Wu, F.-I.; Shu, C.-F. Macromolecules 2007, 40, 247–252.

24 (a) Lee, J.; Lee, J.-I.; Park, M.-J.; Jung, Y. K.; Cho, N. S.; Cho, H. J.; Hwang, D.-H.; Lee, S.-K.; Park, J.-H.; Hong, J.; Chu, H. Y.; Shim, H.-K. J Polym Sci Part A: Polym Chem 2007, 45, 1236–1246; (b) Park, M.-J.; Lee, J.; Jung, I. H.; Park, J.-H.; Hwang, D.-H.; Shim, H.-K. Macromolecules 2008, 41, 9643–9649.

25 Stolka, M.; Janus, J. F.; Pai, D. M. J Phys Chem 1984, 88, 4707–4714.

26 Hwang, D.-H.; Park, M.-J.; Lee, J.-H.; Cho, N.-S.; Shim, H.-K.; Lee, C. Synth Met 2004, 146, 145–150.

27 Pommerehe, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. Adv Mater 1995, 7, 55–58.