Novel Green-Light-Emitting Polymers Based on Cyclopenta[*def*]phenanthrene

Youngeup Jin,[†] Yunna Kim,[†] Sun Hee Kim,[‡] Suhee Song,[†] Han Young Woo,[§] Kwanghee Lee,[‡] and Hongsuk Suh*,[†]

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Korea; Department of Material Science & Engineering, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea; and Department of Nanomaterials Engineering, Pusan National University, Miryang 627-706, Korea

Received April 14, 2008; Revised Manuscript Received June 11, 2008

ABSTRACT: New electroluminescent copolymers with BT units in the PCPP backbone, poly(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)-*co*-poly(2,1,3-benzothiadiazole) (PCPPBTs), have been synthesized by the Suzuki coupling reaction. The BT units were introduced on the PCPP backbone to affect a red-shifted color change and to increase the electron affinities of the copolymers. The PCPPBTs exhibited absorption spectra with maximum peaks at 330−431 nm in THF solution and at 337−445 nm in the solid film state. In the PL spectra were two emission peaks at around 400 and 530 nm in solution and at 510−535 nm in thin film. The PL characteristics of these copolymers could possibly be influenced by two competing effects: Förster energy transfer and the intramolecular charge transfer. The HOMO energy levels of the copolymers were approximately −5.89 to −5.96 eV, and the LUMO energy levels were about −3.33 to −3.50 eV. The polymer LEDs (ITO/PEDOT/polymer/Ca:Al) of PCPPBTs showed emissions with maximum peaks at 508−528 nm. By randomly copolymerizing the BT into the PCPP, the PL efficiency was improved. Among all the devices fabricated, the best device was the one with PCPPBT10, which showed the highest luminous efficiency of 1.25 cd/A and the highest brightness of 1170 cd/m^2. The present study suggests that the introduction of BT units in PCPP can enhance the device performance to result in stable PL and EL spectra with high current density and brightness.

Introduction

For use in full color flat panel displays, organic light-emitting diodes (OLEDs) have emerged as a very promising candidate with several advantages over conventional devices including low driving voltage, wide viewing angle, thin film structure, and a simpler manufacturing process.[1] Numerous reports about polymer light-emitting diodes (PLEDs) have been published since π-conjugated polymeric materials are slated to possess interesting and useful electronic and optical properties after the discovery of electroluminescence (EL) from conjugated polymers.[2–4] A large number of electroactive and photoactive conjugated polymers have been investigated in order to obtain stable high-efficiency RGB emitters during the past few years,[5] such as poly(*p*-phenylenevinylene) (PPV),[6] poly(*p*-phenylene) (PPP),[7] polythiophene (PT),[8] polyfluorene (PF),[9] and poly(2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)) (PCPP)[10,11] because of the prospective application as large-area light-emitting diodes (LEDs).[12–16]

To design polymers with improved functional properties that cannot easily be attained by the corresponding homopolymers, considerable attention has been given to the syntheses and properties of conjugated copolymers in which the characteristics of the comonomers possess a novel means.[17,18] One of the keys in improvement of OLEDs is the discovery of the guest−host doped emitter system.[19] A wide-band-gap host, with optimized transport and luminescent properties such as PFs, and a variety of highly fluorescent or phosphorescent narrow-band gap guest dopants have been used to generate EL of desirable colors with very high efficiencies. Caused by the relatively high reduction potential and electron affinity, 2,1,3-benzothiadiazoles (BTs) are one of the most important moieties among the narrow-band gap comonomers. The HOMO and LUMO levels of conjugated molecules are defined by their ionization potential (IP) and electron affinity (EA), which are associated with electrochemical oxidation and reduction potentials. The BT derivatives can have well-organized crystal structures and efficient fluorophores.[20] There are some reports about copolymers based on fluorene as a donor with various acceptor including benzothiadiazole (BT). The efficient energy transfer due to exciton trapping on narrow-band-gap heterocyclic sites has been observed.[21] Heeger et al. demonstrated highly efficient energy transfer from absorbing band states, PF units, to emitting defect states, BT units, resulting in a substantial spectral separation of absorption and emission and a concomitant lowering of self-absorption losses.[22] The reduction of self-absorption, via fast and efficient Föster energy transfer from an absorbing host to an emitting guest, leads to an increase in the photoluminescence (PL) efficiency.

PCPP with significant enhancement of stability and efficiency with an emission peak at 400 nm was reported by our group. The PLED based on PCPP generates EL emissions with high maximum brightness (1500 cd/m^2 at 14 V), high efficiency (0.70 cd/A at 180 mA/cm^2), maximum peak at 400 nm, low turn-on voltage (6.0 V), and excellent CIE coordinates ($x = 0.17$, $y = 0.12$) for the blue color without any filtering. Moreover, this polymer displays stabilized blue EL emissions without any low-energy emission bands in the region of 500−600 nm even after annealing in air for 18 h at 150 °C or operation of the device in air for 40 min.[10,11] Emission color of PCPP can be changed over an entire visible region by introducing narrow-band-gap comonomers into the PCPP backbone.

The present investigation deals with the synthesis, characterization, photophysics, and EL of new copolymers, poly(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)-*co*-poly(2,1,3-benzothiadiazole) (PCPPBTs). The new copolymers, PCPPBTs, were synthesized by the Suzuki coupling reaction[23] from

---

* To whom correspondence should be addressed. E-mail: hssuh@pusan.ac.kr.

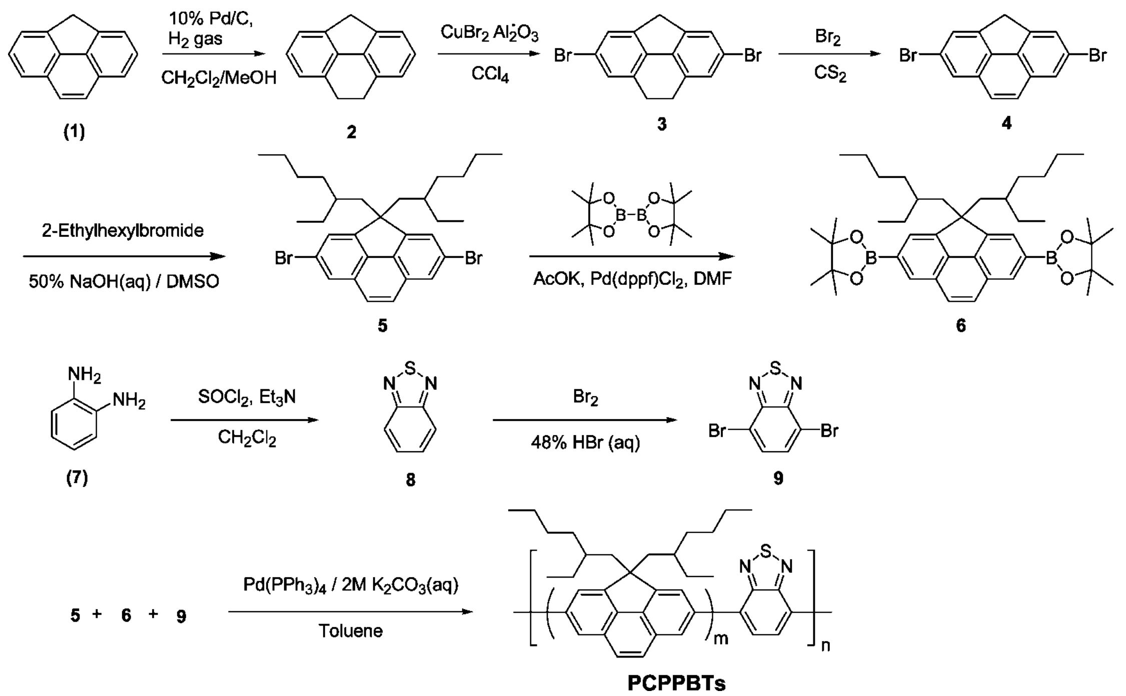
[†] Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University.

[‡] Gwangju Institute of Science and Technology.

[§] Department of Nanomaterials Engineering, Pusan National University.

10.1021/ma800823u CCC: $40.75

Scheme 1. Synthetic Routes for the Monomers and the Polymers



cyclopenta[*def*]phenanthrene (CPP) and BT, as illustrated in Scheme 1. The BT units were introduced into the main chains of PCPP to enhance the electron transport properties and to improve the recombination efficiency of holes and electrons. EL devices fabricated from the synthesized polymers as emissive layers were characterized.

Experimental Section

Materials and Instruments. All reagents were purchased from Aldrich or TCI and used without further purification. Solvents were purified by normal procedure and handled under a moisture-free atmosphere. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Gemini-200 (200 MHz), Unityplus-300 (300 MHz), and Inova-500 (500 MHz) spectrometer, and chemical shifts were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230−400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminum plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. The PL and EL spectra of the device were measured using an Oriel InstaSpec IV CCD detection systems. For PL spectrum measurements, a xenon lamp was used as the excitation source, and the incident beam took the maximum absorption peak of the polymers. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection transport layer, was introduced between an emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. Isopropyl solution of the PEDOT/PSS was spin-coated on the surface-treated ITO substrate. On top of the PEDOT/PSS layer, the emissive polymer film was obtained by spin-casting an ODCB (*o*-dichlorobenzene) solution of the polymer. The prepared emissive polymer thin film prepared had a uniform surface with a thickness of ≈110 nm. The emissive film was dried in vacuum, and calcium (20 nm) and aluminum (100 nm) electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 10^{-7} Torr, yielding active areas of 4 mm^2. For the determination of device characteristics, current−voltage ($I-V$) characteristics were measured using a Keithley 236 source measure unit. All processing steps and measurements mentioned above were carried out under air and at room temperature. To examine electrochemical properties of the resulting polymer, the polymer film was cast from THF solution onto a platinum plate as a working electrode. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) or fast atom bombardment (FAB) conditions in the Korea Basic Science Institute Daegu Branch. Elemental analyses (EA) were performed by Flash EA 1112 Series.

8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene (2). The mixture of 1.45 g (7.62 mmol) of cyclopenta[*def*]phenanthrene (**1**) and 300 mg of 10% palladium−charcoal in 40 mL/40 mL of methanol/dichloromethane was shaken for 15 h at room temperature under a hydrogen atmosphere (60 psi). After removal of the catalyst by filtration, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (30 × 30 mm column, SiO$_2$, 100% of *n*-hexane) to give 1.46 g (99%) of compound **2**: white solid, mp 134 °C, R_f 0.44 (SiO$_2$, hexane 100%). ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 7.37 (d, 2H J = 7.4 Hz), 7.24 (t, 2H J = 7.4 Hz), 7.17 (d, 2H J = 7.4 Hz), 3.92 (s, 2H), 3.18 (s, 4H). ^{13}C NMR (75 MHz, CDCl$_3$): δ (ppm) 140.67, 139.65, 130.76, 127.51, 124.92, 122.95, 37.69, 26.51. HRMS (EI) *m*/*z* 192.0943 (calculated for $C_{15}H_{12}$ 192.0939). Anal. Calcd for $C_{15}H_{12}$: C, 93.71; H, 6.29. Found: C, 94.41; H, 4.79.

2,6-Dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (3). To prepare copper bromide adsorbed on alumina, a solution of 10 g of copper bromide in 30 mL of distilled water was treated with 20 g of neutral alumina (Merck aluminum oxide 90 active neutral) at room temperature. The reaction mixture was concentrated at 80 °C under reduced pressure. The resulting residue was dried under vacuum (4 Torr) at 100 °C for 15 h to generate the copper bromide adsorbed on alumina. To a stirred solution of 1.87 g (3.59 mmol) of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**2**) in 70 mL of carbon tetrachloride at room temperature was added 31.63 g of copper bromide adsorbed on alumina. After 5 h at 60 °C, the solid was filtered and washed with 2 × 30 mL of carbon tetrachloride. The combined organic phase was concentrated under reduced pressure and purified by flash column chromatography (30 × 50 mm column, SiO_2, 100% carbon tetrachloride) to give 3.36 g (99%) of compound **3**: pale yellow solid, mp 184 °C, R_f 0.50 (SiO_2, hexane 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47 (s, 2H), 7.46 (s, 2H), 3.83 (s, 2H), 3.08 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 141.81, 137.56, 131.91, 128.43, 126.43, 121.33, 37.35, 25.95. HRMS (EI) *m/z* 347.9153 (calculated for $C_{15}H_{10}Br_2$ 347.9149). Anal. Calcd for $C_{15}H_{10}Br_2$: C, 51.47; H, 2.88. Found: C, 51.40; H, 1.65.

2,6-Dibromo-4*H*-cyclopenta[*def*]phenanthrene (4). To a stirred solution of 3.15 g (9.05 mmol) of 2,6-dibromo-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**3**) in 70 mL of carbon disulfide at room temperature was added dropwise 0.56 mL (10.85 mmol) of Br_2 in carbon disulfide over 3 h. The reaction mixture was stirred for 1 h, concentrated under reduced pressure, and purified by flash column chromatography (40 × 100 mm column, SiO_2, 100% hexane) to give 3.15 g (100%) of compound **4**: pale yellow solid, mp 210 °C, R_f 0.53 (SiO_2, hexane 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.99 (s, 2H), 7.80 (s, 2H), 7.75 (s, 2H), 4.32 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.03, 132.91, 128.97, 127.97, 126.41, 125.62, 125.31, 37.16. HRMS (EI) *m/z* 345.8993 (calculated for $C_{15}H_8Br_2$ 345.8993). Anal. Calcd for $C_{15}H_8Br_2$: C, 51.77; H, 2.32. Found: C, 52.60; H, 1.85.

2,6-Dibromo-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene (5). To a stirred solution of 3.12 g (8.98 mmol) of 2,6-dibromo-4*H*-cyclopenta[*def*]phenanthrene (**4**) and catalytic amounts of triethylbenzylammonium chloride in 175 mL of DMSO under nitrogen was added 4.79 mL (27.00 mmol) of 2-ethylhexyl bromide. After 1 h at 60 °C, 10 mL of 50% aqueous NaOH was added. The reaction mixture was cooled to room temperature and stirred for 5 h. An excess amount of ethyl acetate was added to the reaction mixture to generate the precipitate the NaOH. After filtering off the precipitated NaOH, the organic layer was washed with 4 × 100 mL of water. The organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (40 × 300 mm column, SiO_2, 100% of *n*-hexane) to give 3.59 g (69.8%) of extremely clean compound **5**: white crystal, mp 44 °C, R_f 0.65 (SiO_2, hexane 100%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.97 (d, 2H $J = 1.1$ Hz), 7.76 (s, 2H), 7.66 (t, 2H $J = 1.1$ Hz), 2.12 (m, 4H), 0.49−0.85 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.96, 135.44, 128.64, 125.90, 125.63, 124.69, 121.86, 59.72, 44.04, 35.46, 34.08, 28.30, 27.55, 22.86, 14.20, 10.54. HRMS (EI) *m/z* 570.1532 (calculated for $C_{31}H_{40}Br_2$ 570.1497). Anal. Calcd for $C_{31}H_{40}Br_2$: C, 65.04; H, 7.04. Found: C, 64.67; H, 7.41.

2-[4,4-Bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-cyclopenta[*def*]phenanthren-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6). Under an argon atmosphere, 2.19 g (3.83 mmol) of dibromo compound **5**, 4.86 g (19.15 mmol) of bis(pinacolato)diboron, 2.26 g (22.98 mmol) of AcOK, and 0.18 g (0.23 mmol) of $Pd(dppf)Cl_2$ were dissolved in 40 mL of DMF and heated to 60 °C overnight. After the reaction mixture was cooled to room temperature, water and diethyl ether were added. The aqueous phase was extracted with diethyl ether, and the combined organic layers were dried over $MgSO_4$. The solvent was removed under vacuum, and the residue was purified by column chromatography (40 × 150 mm column, SiO_2, ethyl acetate:hexane = 1:20) to give 2.0 g (78%) of extremely clean compound **6**: white crystal, mp 97 °C, R_f 0.42 (SiO_2, ethyl acetate:hexane = 1:14). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.31 (s, 2H), 7.98 (s, 0.5H by chirality of 2H), 7.96 (s, 1H by chirality of 2H), 7.94 (s, 0.5H by chirality of 2H), 2.16 (d, 4H $J = 4.67$ Hz), 1.41 (s, 24H), 0.44−0.82 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 149.19, 139.71, 130.79, 128.23, 127.91, 126.04, 125.71, 83.91, 59.04, 44.03, 35.41, 33.98, 28.18, 27.73, 25.14, 22.90, 14.27, 10.61. HRMS (EI) *m/z* 666.4996 (calculated for $C_{43}H_{64}B_2O_4$ 666.5005).

2,1,3-Benzothiadiazole (8). To the mixture of commercially available 10 g (92.47 mmol) of *o*-phenylenediamine (**7**) in 300 mL of CH_2Cl_2 was added 37.44 g (369.98 mmol) of triethylamine. After stirring the mixture to generate the homogeneous solution, thionyl chloride was added dropwise very slowly, and the mixture was refluxed for 4 h. The solvent was removed under reduced pressure, and 700 mL of water was added. Concentrated HCl was added to obtain the pH of 2. The desired compound was distilled by direct steam distillation after addition of water to the mixture. The steam-distilled mixture was extracted three times with 200 mL of CH_2Cl_2, dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography to give 11.71 g (93%) of compound **8**: white solid of needle type, mp 44 °C, R_f 0.5 (SiO_2, ethyl acetate:hexane = 1:10). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.99 (dd, 2H $J = 3.3$, 4.6 Hz), 7.57 (dd, 2H $J = 3.1$, 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 154.6, 129.1, 122.4. HRMS (EI) *m/z* 136.0099 (calculated for $C_6H_4N_2S$ 136.0095).

4,7-Dibromo-2,1,3-benzothiadiazole (9). To the solution of 10 g (73.44 mmol) of benzothiadiazole (**8**) in 150 mL of HBr (48%) was added dropwise 35.21 g (220.32 mmol) of a solution Br_2 in 100 mL of HBr (48%) very slowly. After refluxing for 6 h, an orange solid precipitated. The mixture was allowed to cool to room temperature, and saturated solution of $NaHSO_3$ was added to neutralize the residual amount of Br_2. The mixture was filtered and washed exhaustively with water. The solid was then washed once with cold diethyl ether and purified by flash chromatography to give 20.51 g (95%) of compound **9**: white solid of needle type, mp 167 °C, R_f 0.4 (SiO_2, ethyl acetate:hexane = 1:4). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.73 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): δ (ppm): 152.6, 132.1. 113.6. HRMS (EI) *m/z* 291.8310 (calculated for $C_6H_2Br_2N_2S$ 291.8305).

Poly(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)-*co*-poly(2,1,3-benzothiadiazole) (PCPPBTs). PCPPBTs with various feed ratios of CPP and BT contents were synthesized. Carefully purified 2,6-dibromo-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene (**5**), 2-[4,4-bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-cyclopenta[*def*]phenanthren-2-yl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**), 4,7-dibromo-2,1,3-benzothiazole (**9**), and $(PPh_3)_4Pd(0)$ (3 mol %) were dissolved in a mixture of toluene and aqueous 2 M Na_2CO_3. The mixture was refluxed with vigorous stirring for 3 days under argon atmosphere. After the mixture was cooled to room temperature, it was poured into methanol. The precipitated material was recovered by filtration. The resulting solid material was reprecipitated using 100 mL of THF/1.0 L of methanol several times to remove catalyst residues and to generate PCPPBTs: PCPPBT0.5 (copolymer with 0.5 mol % BT in the feed), PCPPBT01 (copolymer with 1 mol % BT in the feed), PCPPBT03 (copolymer with 3 mol % BT in the feed), PCPPBT05 (copolymer with 5 mol % BT in the feed), PCPPBT10 (copolymer with 10 mol % BT in the feed), PCPPBT20 (copolymer with 20 mol % BT in the feed), PCPPBT30 (copolymer with 30 mol % BT in the feed), and PCPPBT50 (copolymer with 50 mol % BT in the feed)). The yields of the polymers ranged from 48 to 57%. The resulting polymers were soluble in THF, $CHCl_3$, *o*-dichlorobenzene (ODCB), and toluene. To obtain copolymers of other composition, the BT content in the feed mixture was adjusted. The nitrogen contents for each copolymer, obtained from elemental analysis, were used for the calculation of actual copolymer composition. Elemental anal. calcd for PCPPBT50 (copolymer from 50 mol % BT in the feed): C, 81.27%; H, 7.74%; N, 5.12%. Found for PCPPBT50: C, 80.47%; H, 8.19%; N, 4.19%; for PCPPBT30 (copolymer from 30 mol % BT in the feed): C, 79.63%; H, 8.24%; N, 2.58%; for PCPPBT10 (copolymer from 10 mol % BT in the feed): C, 85.57%; H, 9.31%; N, 0.75%; for PCPPBT5 (copolymer from 5 mol % BT in the feed): C, 86.54%; H, 9.69%; N, 0.42%; for PCPPBT3 (copolymer from 3 mol % BT in the feed): C, 87.28%; H, 9.82%; N, 0.25%; for PCPPBT1 (copolymer from 1 mol % BT in the feed): C, 88.26%; H, 9.91%; N, 0.12%; for PCPPBT0.5 (copolymer from 0.5 mol % BT in the feed): C, 88.19%; H, 9.75%; N, 0.10%.

Results and Discussion

Synthesis and Characterization of Polymers. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. 2,6-Dibromo-4*H*-cyclopenta[*def*]phenan-

Table 1. Characterization of the PCPPBTs

polymer	PCPP:BT in the feed composition	PCPP:BT in the copolymers[a]	M_n[b] ($\times 10^3$)	M_w[b] ($\times 10^3$)	PDI[b]	T_g[c] (°C)	T_d[d] (°C)
PCPPBT0.5	99.5:0.5	99.0:1.0	11	44	4.02	81	400
PCPPBT1	99:1	98.8:1.2	13	53	3.99	82	398
PCPPBT3	97:3	97.6:2.4	13	46	3.49	83	398
PCPPBT5	95:5	95.9:4.1	11	47	4.28	84	396
PCPPBT10	90:10	92.7:7.3	20	29	1.45	84	407
PCPPBT30	70:30	74.8:25.2	13	22	1.69	98	398
PCPPBT50	50:50	59.1:40.9	31	91	2.87	115	400

[a] Calculated from the results of elemental analysis. [b] Molecular weight (M_n, M_w) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. [c] Glass transition temperature measured by DSC under N_2. [d] Onset decomposition temperature (5% weight loss) measured by TGA under N_2.

threne (**1**) was reacted with 2-ethylhexyl bromide, catalytic amounts of triethylbenzylammonium chloride in DMSO, and 50% aqueous NaOH to obtain 2,6-dibromo-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene (**2**). Bis(pinacolato)diboron was reacted with dibromo compound **2** using catalytic amounts of Pd(dppf)Cl_2 and potassium acetate in DMF to obtain 2-[4,4-bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-cyclopenta[*def*]phenanthren-2-yl]-4,4 (**3**). Commercially available *o*-phenylenediamine (**7**) was treated with freshly distilled thionyl chloride in the presence of triethylamine in CH_2Cl_2 to afford 2,1,3-benzothiadiazole (**5**) after steam distillation. Upon reaction with molecular bromine (added dropwise, very slowly) in hydrobromic acid, compound **5** gives exclusively the 4,7-dibromo-2,1,3-benzothiazole (**6**). Monomer **6** was copolymerized with monomer **3** by using palladium-catalyzed Suzuki coupling methods.[21] The 50:50 feed ratio of **3** and **6** generated the alternating copolymer poly(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)-*alt*-poly(2,1,3-benzothiadiazole) (PCPPBT50). To generate the copolymers, poly(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene)-*co*-poly(2,1,3-benzothiadiazole), different ratios of **2**, **3**, and **6** were used. The feed ratios of PCPP and BT fragments were 70:30, 90:10, 95:5, 97:3, 99:1, and 99.5:0.5 for the syntheses of PCPPBT30, PCPPBT10, PCPPBT05, PCPPBT03, PCPPBT01, and PCPPBT0.5, respectively.

Table 1 summarizes the polymerization results including molecular weights, PDI, and thermal stability of the copolymers. The number-average molecular weight (M_n) of 11 000−31 000 and weight-average molecular weight (M_w) of 44 000−91 000 with PDI (polydispersity index, M_w/M_n) of 1.45−4.28 of the resulting polymers were determined by gel permission chromatography. The DSC data of the copolymers were obtained at a heating increase rate of 10 °C/min under flowing nitrogen, and the thermal properties were determined by TGA measurements. These copolymers showed good thermal stability with high glass transition temperature (T_g) of 81−115 °C and onset decomposition temperature (T_d, 5% weight loss) of 398−407 °C under nitrogen, which could be advantageous for the PLED device fabrication.

Optical Absorption Properties. The optical absorption and photoluminescence (PL) properties of the copolymers were investigated in both THF solutions and thin solid films. The concentration of all the THF solutions of the copolymers was fixed at 1×10^{-5} M. Transparent and uniform copolymer films were prepared on quartz plates by spin-casting from their respective ODCB solution at room temperature. The absorption and emission data for the copolymers are summarized in Table 2. As shown in Figure 1, there is little difference between the absorption spectra of the solutions and the thin films of the copolymers, which can be attributed to the $\pi-\pi^*$ transitions of the copolymers. The copolymers exhibited maximum absorption peaks at 330−431 nm in THF solution and at 337−445 nm in the solid film state, with the absorption peak at around 300 nm due to the $\pi-\pi^*$ transition of CPP units. PCPPBTs are expected to be useful for the tuning of the emission colors by the adjustment of the ratios of BT units which influence the effective conjugation length. Two distinct absorption bands are observed both in the solution and in the solid states. With increased BT ratios, the induced effective conjugation length by BT units was enlarged and the effective conjugation length by the conjugated main chains of PCPP was decreased. When compared with the absorption spectrum of pure PCPP, the absorption peak appearing at around 350 nm is due to the conjugated main chains of PCPP.[10,11] For the copolymer of PCPPBT50 and PCPPBT30, the peaks by the conjugated main chains of PCPP disappeared or were more blue-shifted than those of the other copolymers, which is probably caused by the change of the effective conjugation length. A long wavelength absorption band at around 450 nm, which increased linearly with increasing BT contents, can be attributed to the BT unit incorporated into the PCPP main chain. The copolymers with 1% and 0.5% BT contents showed almost no peak around this reason.

Table 2. Characteristics of the UV−vis Absorption, Photoluminescence, and Electroluminescence Spectra

polymer	in solution Abs λ_{max} (nm)	in solution PL λ_{max} (nm)	in solution QE_{PL} (%)	in thin film Abs λ_{max} (nm)	in thin film PL λ_{max} (nm)	in thin film QE_{PL} (%)	EL λ_{max} (nm)
PCPPBT0.5	350	395, 529	95	354	413, 510	14.80	508
PCPPBT1	348	395, 529	94	354	411, 519	10.89	508
PCPPBT3	348, 423	394, 534	93	355, 328	411, 519	11.99	508
PCPPBT5	346, 423	394, 534	91	347, 328	410, 526	1.97	512
PCPPBT10	345, 423	394, 534	98	346, 428	420, 528	10.76	516
PCPPBT30	330 429	533	78	337, 440	521	4.24	522
PCPPBT50	431	528	53	445	535	2.32	528

Photoluminescence Properties. Figure 2 shows the PL spectra of the copolymers with the excitation of 350 nm in

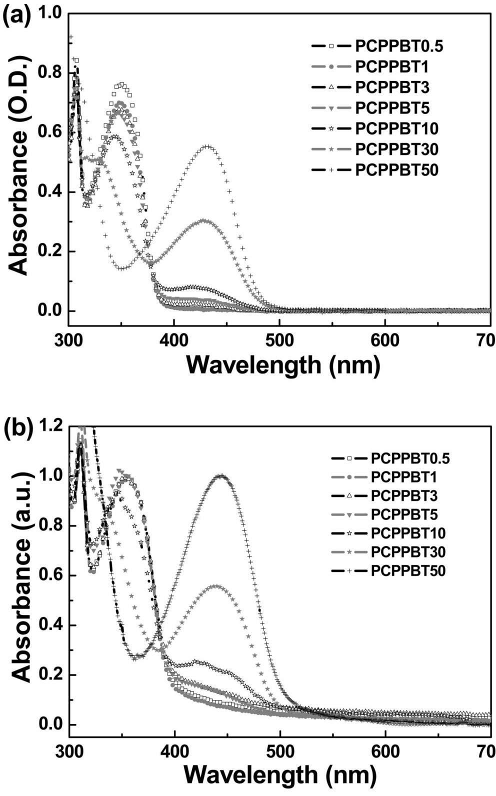


Figure 1. UV−vis absorption of PCPPBTs in chloroform solution at a concentration of 1×10^{-5} mol/L (a) and in thin film (b).

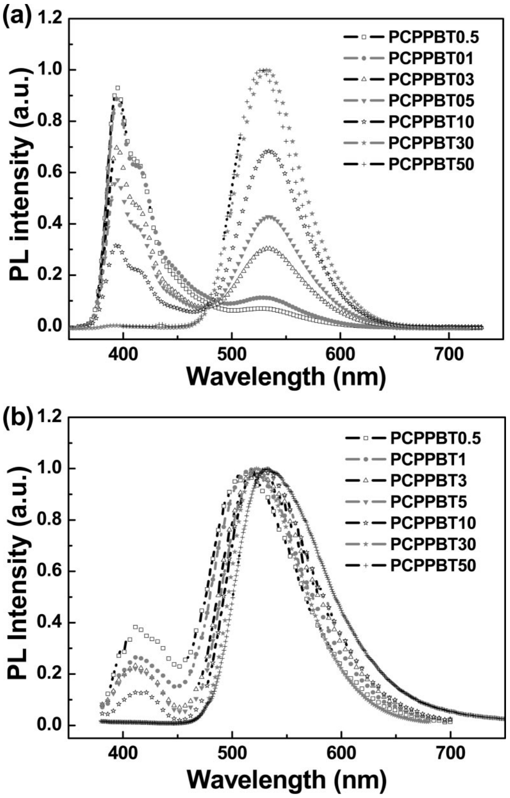


Figure 2. Photoluminescence spectra of PCPPBTs in chloroform solution at a concentration of 1×10^{-5} mol/L (the sum of two maximum peaks is 1) (a) and in thin film (b) with 350 nm excitation.

chloroform and in thin film, respectively. In the chloroform solution, with the copolymer concentration of 1×10^{-5} mol/L, all the copolymers, except PCPPBT30 and PCPPBT50, showed two PL emission peaks at around 400 and 530 nm. The intensity of the emission at around 400 nm decreased with increasing BT contents in the copolymers, while the intensity of the green emission peak at 530 nm increased with increasing BT contents. Therefore, the emission at 400 nm can be assigned to the emission of the PCPP segment in the copolymer, and the emission at 530 nm can be assigned to the emission of the BT unit. For copolymers with over 10%, the PL emissions were dominated by the BT unit, and an emission from the PCPP segments gradually decreased with the increase of the BT contents. The PL characteristics of these copolymers could be influenced by two competing effects: Förster energy transfer and intramolecular charge transfer. Increasing amounts of the BT contents enhances the energy transfer from the PCPP to BT segments, which causes the enhancement of the long wavelength peak. The PL spectra of PCPPBT30 and PCPPBT50 consist of a typical vibronically structured band, exhibiting maximum peaks at 528 nm. The emissive colors were green, and the peaks by PCPP segments were completely quenched, which were attributed to the energy transfer a from PCPP to BT.

In thin film, the PL spectra of PCPPBTs exhibits maximum peaks at 510−535 nm. The emissive colors were green, and the peaks by the PCPP segment were nearly quenched, which was attributed to the facile energy transfer from PCPP to BT as compared to solution conditions, since increasing interchain interaction between polymer backbones. As the BT contents increase in the copolymer system, the emission peaks of PCPPBTs in thin film are red-shifted from 510 to 535 nm. Such a red shift for the copolymer system could be attributed to the increase of the effective conjugation length of the copolymers due to electron-withdrawing BT units. The PL efficiencies, which were measured in the integrating sphere in chloroform solution with an anthracene standard, are listed in Table 2.

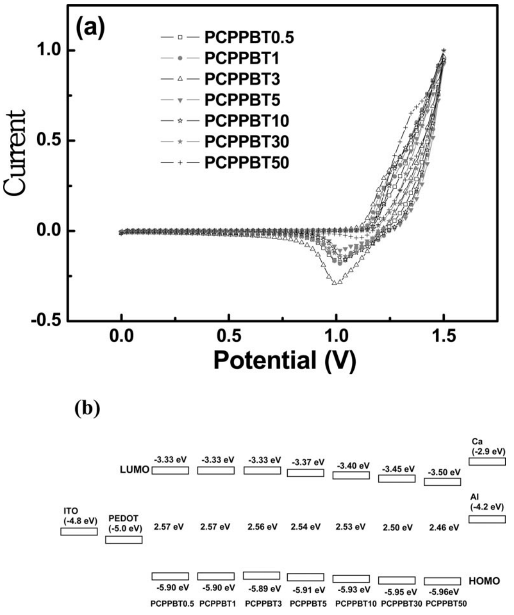


Figure 3. Electrochemical properties (a) and energy band diagrams (b) of PCPPBTs.

Table 3. Electrochemical Potentials and Energy Levels of the Copolymers

polymers	E_{onset}[a] (V)	HOMO[b] (eV)	LUMO[c] (eV)	E_g[d] (eV)
PCPPBT0.5	1.14	−5.90	−3.33	2.57
PCPPBT1	1.14	−5.90	−3.33	2.57
PCPPBT3	1.13	−5.89	−3.33	2.56
PCPPBT5	1.15	−5.91	−3.37	2.54
PCPPBT10	1.17	−5.93	−3.40	2.53
PCPPBT30	1.19	−5.95	−3.45	2.50
PCPPBT50	1.2	−5.96	−3.50	2.46

[a] Onset oxidation potential measured by cyclic voltammetry. [b] Calculated from the oxidation potentials. [c] Calculated from the HOMO energy levels and E_g. [d] Energy band gap was estimated from the onset wavelength of the optical absorption.

Electrochemical Properties. The electrochemical properties of the copolymers were determined from the band gaps estimated from the absorption edges and the HOMO energy levels, which were estimated from the cyclic voltammetry (CV). The CV was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under the protection of argon. A platinum electrode (~0.05 cm^2) coated with a thin polymer film was used as the working electrode. Pt wire and a Ag/AgNO$_3$ electrode were used as the counter and reference electrode, respectively. The energy level of the Ag/AgNO$_3$ reference electrode (calibrated by the FC/FC$^+$ redox system) was 4.76 eV below the vacuum level. The CV spectra are shown in Figure 3, and the oxidation potentials derived from the onset of electrochemical p-doping are summarized in Table 3. HOMO levels were calculated according to the empirical formula ($E_{\mathrm{HOMO}} = -([\mathrm{E_{onset}}]^{\mathrm{ox}} + 4.76)$ (eV).[25,26] During the anodic scan, the oxidation onset potentials of PCPPBTs were in the range of 1.13−1.20 V and exhibited irreversible p-doping process. This peak is under the influence of BT segments. BT has an ionization potential measured by cyclic voltammetry of 5.90 eV and an optical gap of 2.4 eV.[27] HOMO energy levels of the present copolymers are about −5.89 to −5.96 eV. The HOMO energy levels of these copolymers are similar, and all the polymers have high electron-withdrawing effect due to the incorporation of the electron-deficient BT moiety. In the case of PCPPBT50, the HOMO energy level was the most decreased,

Table 4. Device Performance Characteristics of PCPPBTs

the feed ratio of copolymers	turn-on voltage[a] (V)	voltage[b] (V)	current density[b] (mA/cm^2)	luminance[b] (cd/m^2)	LE$_{max}$[c] (cd/A)	CIE (x,y)[d]
PCPPBT0.5	12	21	300	170	0.07	(0.29, 0.37)
PCPPBT1	12	19	150	84	0.06	(0.29, 0.45)
PCPPBT3	11.5	25	544	634	0.15	(0.30, 0.51)
PCPPBT5	8.5	17	187	126	0.12	(0.30, 0.54)
PCPPBT10	8.5	14	108	1170	1.25	(0.30, 0.58)
PCPPBT30	5	9	569	1000	0.30	(0.34, 0.58)
PCPPBT50	6	9	447	1169	0.35	(0.36, 0.58)

[a] Voltages required to achieve a brightness of 1 cd/m^2. [b] Measured under the condition of maximum brightness. [c] Maximum luminescence efficiency. [d] Calculated from the EL spectrum.

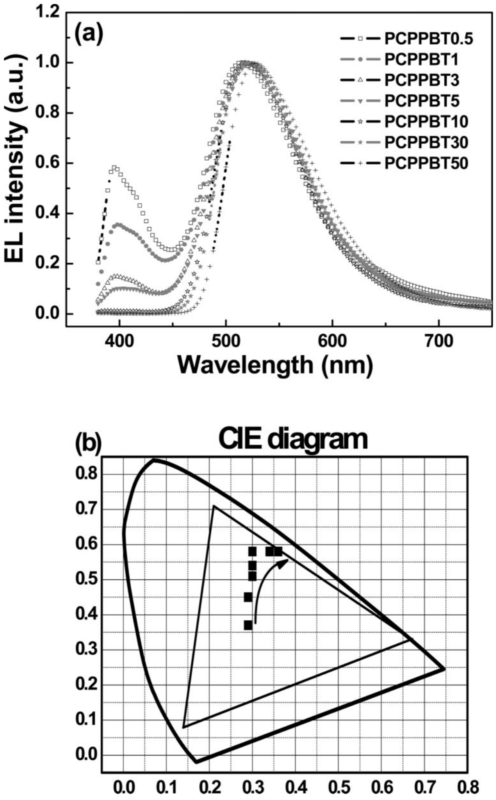


Figure 4. Electroluminescence spectra (a) and CIE coordinates diagram (b) of devices of PCPPBTs with the configuration of ITO/PEDOT/polymer/Ca:Al.

caused primarily by the electron attractive effect of the large number of BT units. The absorption onset wavelengths of PCPPBTs in the film state were 483−505 nm, which correspond to band gaps of 2.46−2.57 eV. The LUMO energy level was calculated from the values of the band gap and HOMO energy level, and the values are about −3.33 to −3.50 eV.

Electroluminescence Properties. The electroluminescence (EL) performance of the copolymers was examined in the device configuration of ITO/PEDOT:PSS/polymer/Ca:Al. Typical EL spectra from such a device are shown in Figure 4. The EL spectra of the polymers were nearly the same as the PL of the polymers, indicating that the EL and PL phenomena originated from the same excited state. Similar to PL emission in the solid state, EL emission spectra showed dominant peaks of the BT unit at around 530 nm. In the case of PCPPBT50, PCPPBT30, and PCPPBT10, the peak at around 400 nm attributed to the PCPP segment is completely quenched, which indicates that energy transfer from the PCPP segment to the BT unit is a very efficient process. For these copolymers, energy transfer probably occurs mainly within the polymer chain via an intra- and intermolecular trapping mechanism. The PCPP homopolymer has a deep-blue EL emission (CIE = 0.17, 0.12) with EL emission maximum at 400 nm.[10,11] The chromaticity coordinates changed from $x = 0.36$, $y = 0.58$ for PCPPBT50 to $x = 0.29$, $y = 0.37$ for PCPPBT0.5. In the case of PCPPBT50, the EL spectra showed maximum peak at 528 nm, which was the most red-shifted. In the case of PCPPBT50, PCPPBT30, and PCPPBT10, the EL emission color remained green and stable over the operating voltage range of the diode without variation of the CIE coordinates as shown in Figure 5. In the case of the copolymers with low ratio of BT units, the initial EL spectrum showed a minor peak at around 400 nm. With increased current density, the spectra were changed to green and stabilized over the operating voltage range of the diode without variation of the CIE coordinates similar to the cases of copolymers with high ratios of BT units.

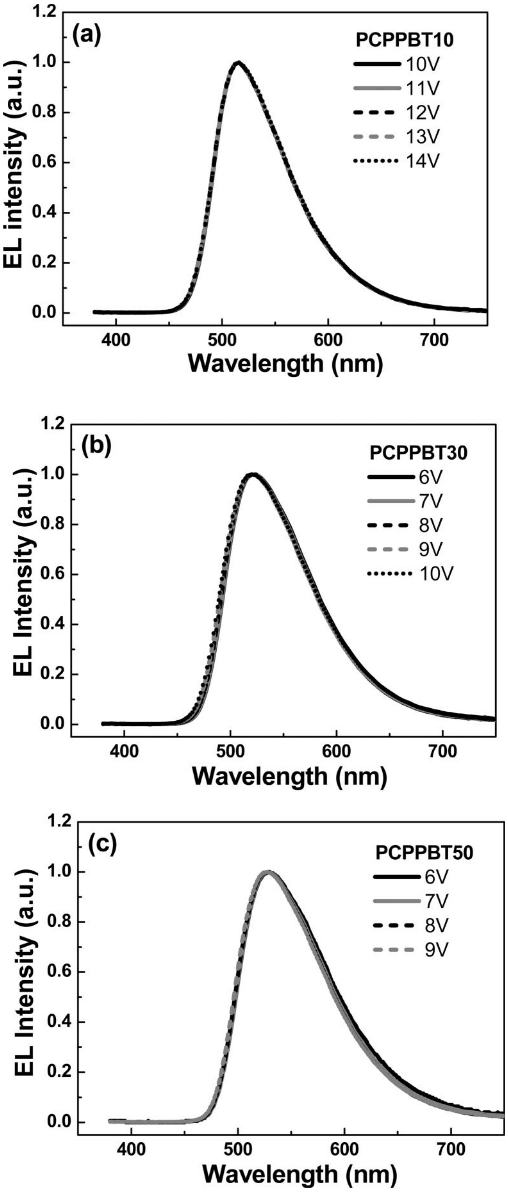


Figure 5. Color stability of devices (PCPPBT10 (a), PCPPBT30 (b), and PCPPBT50 (c)) with the configuration of ITO/PEDOT/polymer/Ca:Al at various voltages.

Current Density−Voltage−Luminescence (*J*−*V*−*L*) Characteristics. The luminescence−voltage (*V*−*L*) characteristics of ITO/PEDOT/polymer/Ca:Al devices are shown in Figure 6a. The copolymers with higher BT units can have lower turn-on voltage and higher current density and brightness due to

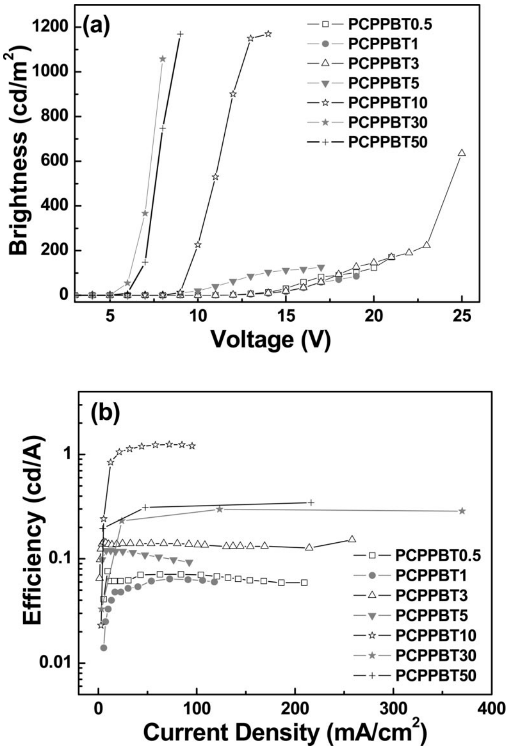


Figure 6. (a) Voltage−luminescence (*V*−*L*) characteristics and (b) efficiencies of OLEDs of PCPPBTs with the configuration of ITO/PEDOT/polymer/Ca:Al.

increasing electron injection ability, caused by the presence of the BT units. The turn-on voltages of ITO/PEDOT/polymer/Ca:Al devices were about 5−12 V. The luminescence intensities of the polymers increased with an increase in voltage; the maximum luminescence (L_{max}) of PCPPBT10 was 1170 cd/m^2 at 14 V.

As shown in Figure 6b, the luminescence efficiencies of the copolymers at room temperature were between 0.06 and 1.25 cd/A. Among all the devices fabricated, the best device was the one with PCPPBT10, exhibiting the highest luminous efficiency of 1.25 cd/A, even higher than that of PCPP homopolymer (0.7 cd/A).[10,11] It seems that the reduction of self-absorption, via fast and efficient Föster energy transfer from the absorbing host polymer (PCPP) to an emitting guest material (BT), leads to an increase in electroluminescence (EL) efficiency for PCPPBT10. PCPP derivatives have been reported as new stable conjugated backbones with high efficiencies. The introduction of BT units in PCPPs can get good merits, which show color change and high brightness since BT units induce electron-attracting effects. Therefore, we conclude that the introduction of the BT units in PCPPs can enhance the device performance to result in stable PL and EL spectra with high current density and brightness.

Conclusion

The donor−acceptor copolymers, PCPPBTs, were synthesized by the Suzuki coupling reaction. The experimental results suggest that the acceptor contents affect the electronic and optoelectronic properties including the optical band gap, LUMO level, and luminescence maximum. The copolymers exhibited maximum absorption peaks at 330−431 nm in THF solution and 337−445 nm in the solid film state. In the PL spectra were two PL emission peaks at around 400 and 530 nm in solution. The intensities of the blue-emitting peaks were decreased, while those of the green-emitting peaks were increased. The PL characteristics of these copolymers could be influenced by two competing effects: Förster energy transfer and intramolecular charge transfer. In thin film, the PL spectra of PCPPBTs exhibited maximum peaks at 510−535 nm. The emissive colors were green and the peaks by the PCPP segments were nearly quenched. The HOMO energy levels of the copolymers ranged from −5.89 to −5.96 eV, and the LUMO energy levels were about −3.33 to −3.50 eV. The polymer LEDs of PCPPBTs with the configuration of ITO/PEDOT/polymer/Ca:Al emitted light with maximum peaks at 508−528 nm. Among all the devices fabricated, the best device was the one with PCPPBT10, which showed the highest luminous efficiency of 1.25 cd/A and the highest brightness of 1170 cd/m^2. The present study suggests that the tuning of the electronic and optoelectronic properties could be achieved by incorporating the acceptor, BT, contents into the PCPP.

Acknowledgment. This work was supported by the Ministry of Information & Communications, Korea, under the Information Technology Research Center (ITRC) Support Program and International Cooperation Research Program of the Ministry of Science & Technology, Korea (Global Research Laboratory, M6-0605-00-0005).

References and Notes

(1) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv. Mater.* **2000**, *12*, 1737.
(2) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller, J.; Moon, R.; Roitman, D. B.; Stoching, A. *Science* **1996**, *273*, 884.
(3) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Santos, D. A.; Bredas, J. L.; Lõgdlund, M.; Salameck, W. R. *Nature (London)* **1999**, *357*, 121.
(4) Mikroyannidis, J. A.; Gibbons, K. M.; Kulkarni, A. P.; Jenekhe, S. A. *Macromolecules* **2008**, *41*, 663.
(5) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.
(6) 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 (London)* **1990**, *347*, 539.
(7) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *69*, 934.
(8) Pei, J.; Yu, W. L.; Ni, J.; Lai, Y. H.; Huang, W.; Heeger, A. J. *Macromolecules* **2001**, *34*, 7241.
(9) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.
(10) Suh, H.; Jin, Y.; Park, S. H.; Kim, D.; Kim, J.; Kim, C.; Kim, J. Y.; Lee, K. *Macromolecules* **2005**, *38*, 6285.
(11) Park, S.; Jin, Y.; Kim, S.; Kim, J.; Suh, H.; Lee, K. *Adv. Funct. Mater.* **2007**, *17*, 3063.
(12) Huang, F.; Hou, L.; Wu, H.; Wang, X.; Shen, H.; Cao, W.; Yang, W.; Cao, Y. *J. Am. Chem. Soc.* **2004**, *126*, 9845.
(13) Cho, H. J.; Jung, B. J.; Cho, N. S.; Lee, J.; Shim, H. K. *Macromolecules* **2003**, *36*, 6704.
(14) Grisorio, R.; Suranna, G. P.; Mastrorilli, P.; Nobile, C. F. *Org. Lett.* **2007**, *9*, 3149.
(15) Jin, Y.; Kim, K.; Park, S. H.; Song, S.; Kim, J.; Jung, J.; Lee, K.; Suh, H. *Macromolecules* **2007**, *40*, 6799.
(16) Jin, Y.; Kim, J.; Lee, S.; Kim, J. Y.; Park, S. H.; Lee, K.; Suh, H. *Macromolecules* **2004**, *37*, 6711.
(17) Ng, S. C.; Lu, H. F.; Chan, H. S. O.; Fuji, A.; Laga, T.; Yoshin, K. *Adv. Mater.* **2000**, *12*, 1122.
(18) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 6806.
(19) Tang, C. W.; VanSlyke, S. A.; Chen, C. H. *J. Appl. Phys.* **1989**, *65*, 3610.
(20) Neto, B. A. D.; Lopes, A. S.; Ebeling, G.; Goncalves, R. S.; Costa, V. E. U.; Quina, F. H.; Dupont, J. *Tetrahedron* **2005**, *61*, 10975.
(21) Burns, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gywer, R. W. *Nature (London)* **1992**, *356*, 47.
(22) Vehse, M.; Liu, B.; Edman, L.; Bazan, G. C.; Heeger, A. J. *Adv. Mater.* **2004**, *16*, 1001.
(23) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
(24) Mitsuo, K.; Hiroaki, S.; Suehiko; Y., *J. Org. Chem.* **1988**, *53*, 2093.
(25) Jin, S.-H.; Kim, M.-Y.; Kim, J. Y.; Lee, K.; Gal, Y.-S. *J. Am. Chem. Soc.* **2004**, *126*, 2474.
(26) Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53.
(27) Campbell, A. J.; Bradley, D. D. C.; Antoniadis, H. *Appl. Phys. Lett.* **2001**, *79*, 2133.

MA800823U