

Synthesis and Characterization of Novel Conjugated Polymer with Thiophene and Benzimidazole[†]

Suhee Song, Sung Heum Park,^{*,¶} Youngeup Jin,[§] Il Kim,[#] Kwanghee Lee,[¶] and Hongsuk Suh^{*}

Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Korea *E-mail: hssuh@pusan.ac.kr

[‡]Department of Physics, Pukyong National University, Busan 608-739, Korea

[§]Department of Industrial Chemistry, Pukyong National University, Busan 608-739, Korea

[#]The WCU Center for Synthetic Polymer Bioconjugate Hybrid Materials, Department of polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

[¶]Department of Materials Science and Engineering Gwangju Institute of Science and Technology, Gwangju 500-712, Korea
Received March 14, 2011, Accepted June 8, 2011

The synthesis of copolymers containing thiophene and benzimidazole unit by Stille polymerization is reported. The polymers with many unsubstituted thiophene units in the backbone have been reported to show low solubility, which has been a problem for spin-coating for the device fabrication. In dihexyl-2*H*-benzimidazole, the sulfur at 2-position of BT unit was replaced with dialkyl substituted carbon, while keeping the 1,2-quinoid form, to improve the solubility of the polymers. The PL emission spectra of the PHBIT1, PHBIT2 and PHBIT3 in chloroform solutions show maximum peaks at 500 ~ 561 nm. In thin films, maximum peaks of the PHBITs appeared at 529, 562 and 569 nm, respectively. The EL emission maxima of the PHBIT1 and PHBIT2 appear at around 588 and 576 nm, respectively. The current density and maximum luminescence of the LED with the configuration of ITO/PEDOT/PHBIT2/Ca/Al are 552 mA/cm² and 46 cd/m², respectively.

Key Words : Polymer, PLED, Thiophene, Benzimidazole

Introduction

The conjugated polymers have been researched for numerous applications in electronic and optoelectronic devices including light-emitting diodes (LEDs),¹⁻⁵ organic thin film transistor (OTFT),⁶ and organic photovoltaic devices (OPVs).⁷ The major advantage of conjugated polymers is their tunable emission colors, which has been realized by appropriate modification of the molecular structures to control the effective conjugation lengths.⁸ In the area of polymer-based LEDs, much interest has been paid to conjugated polymers with various templates⁹ such as poly(phenylenevinylene) (PPV),¹⁰ poly(thiophene),¹¹ poly(fluorene),¹² and poly(cyclopentaphenanthrene).¹³⁻¹⁴ Poly(3-hexylthiophene) (P3HT), the thiophene-based conjugated polymer, is one of the most widely used materials in OLEDs, OPVs and OTFTs.¹⁵⁻¹⁷

The alkyl substituted thiophenes, including P3HT, have been shown blue shifted emission, which is attributed to a reduction of the effective conjugation length by steric repulsion between the H atom in 4-position of neighboring thiophene and H atom of the first methylene unit of the alkyl chain. Although the alkyl substitution results in steric interactions to provide decreased backbone planarity, it enhances the solubility of the polymers to provide adequate processability for spin-coating and possibly for inkjet

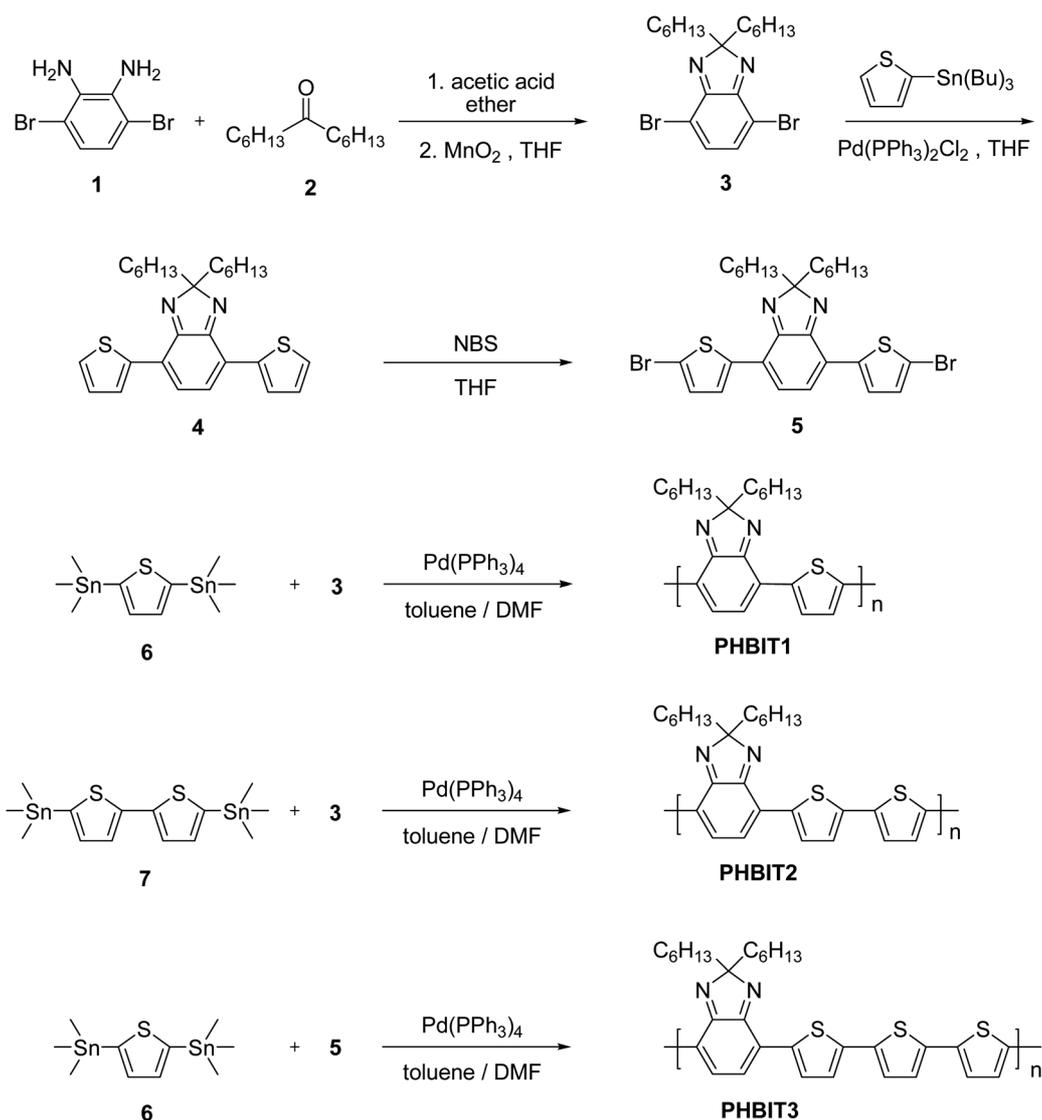
printing.¹⁸ Previously, we reported that the substitution of the BT unit of poly[*N*-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) with dihexyl-2*H*-benzimidazole increased the solubility of the corresponding polymer. In dihexyl-2*H*-benzimidazole, the sulfur at 2-position of BT unit was replaced with dialkyl substituted carbon, while keeping the 1,2-quinoid form by using 2*H*-benzimidazole unit, to improve the solubility of the polymers.¹⁹⁻²⁰

In this paper, it is reported that new polymers, poly(4,7-(2,2-dihexyl-2*H*-benzimidazole)-*co*-5,5-(thiophene)) (PHBIT1), poly(4,7-(2,2-dihexyl-2*H*-benzimidazole)-*co*-5,5'-(2,2'-bithiophene)) (PHBIT2) and poly(4,7-(2,2-dihexyl-2*H*-benzimidazole)-*co*-5,5'-(2,2':5',2''-terthiophene)) (PHBIT3) were synthesized by Stille coupling reactions of 2,2-dihexyl-2*H*-benzimidazole and thiophene (or bithiophene/terthiophene). Even with unsubstituted thiophene units in the copolymers to facilitate absorption at the longer wavelength region, the incorporation of dihexyl-substituted 2*H*-benzimidazole provided suitable solubility of the resulting polymers.²¹ The electroluminescence properties of the polymers were investigated by fabrication of the OLEDs with the configuration of ITO/PEDOT:PSS/polymer/Ca:Al.

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. In the first step, 3,6-dibromobenzene-1,2-diamine

[†]This paper is dedicated to Professor Eun Lee on the occasion of his honourable retirement.



Scheme 1. Synthetic routes for PHBIT1, PHBIT2 and PHBIT3.

Table 1. Polymerization Results and Thermal Properties of Polymers

Polymer	M_n^a	M_w^a	PDI ^a	DSC (T_g) ^b	TGA (T_d) ^c
PHBIT1	5700	9500	1.66	84	383
PHBIT2	10400	19500	1.88	95	376
PHBIT3	—	—	—	115	442

^aMolecular weight (M_w) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. ^bGlass transition temperature measured by DSC under N_2 . ^cOnset decomposition temperature (5% weight loss) measured by TGA under N_2 .

(1) was treated with 7-tridecanone (2) and acetic acid followed by MnO_2 to generate 2,2-dihexyl-2H-benzimidazole (3), which was coupled with tributyl(2-thienyl)stannane by using dichlorobis(triphenylphosphine)palladium (II) to give 2,2-dihexyl-4,7-di(2-thienyl)-2H-benzimidazole (4). Compound 4 was brominated by *N*-bromosuccinimide (NBS) to provide monomer 4,7-bis(5-bromo-2-thienyl)-2,2-dihexyl-2H-benzimidazole (5). Compound 3 and 2,5-bis(trimethylstannyl)thiophene (6) were co-polymerized through Stille coupling reaction with Pd(0)-catalyst to yield PHBIT1.

Compound 3 and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (7) (or compound 5 and compound 6) were copolymerized under the same conditions to yield PHBIT2 (or PHBIT3). The structures and purities of the monomers were confirmed by 1H -NMR, ^{13}C -NMR, and HRMS. The synthesized polymers were soluble in various organic solvents such as chloroform, chlorobenzene, tetrahydrofuran (THF), dichloromethane and *o*-dichlorobenzene (ODCB).

Table 1 summarizes the polymerization results including molecular weights, PDI (poly dispersity index, M_w/M_n), and

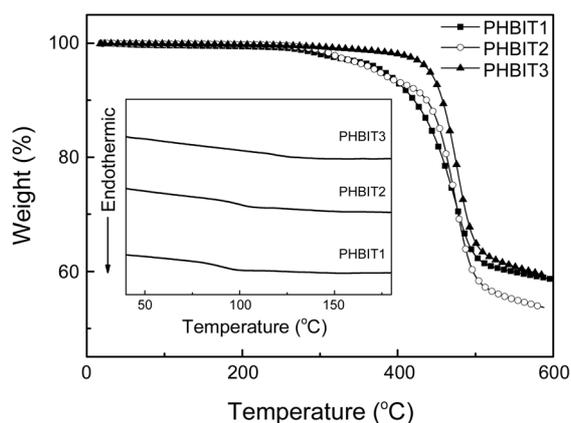


Figure 1. Thermogravimetric analysis of the polymers under N_2 . Inner: Differential scanning calorimetry of the polymers under N_2 .

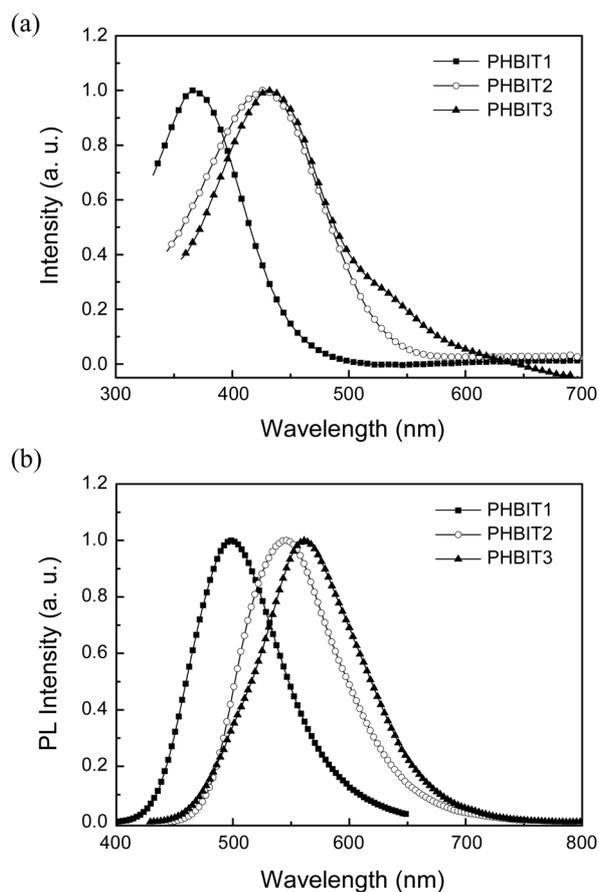


Figure 2. UV-vis absorption (a) and photoluminescence (b) spectra of polymers in the chloroform solution.

thermal stability of the copolymers. The number-average molecular weights (M_n) of 5700 and 10400 and weight-average molecular weights (M_w) of 9500 and 19500 with PDI values of 1.7 and 1.9 were determined by gel permeation chromatography (GPC) for the PHBIT1 and PHBIT2, respectively. The molecular weight of PHBIT3 could not be measured due to low solubility. The thermal properties of the polymers were characterized by both differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA).

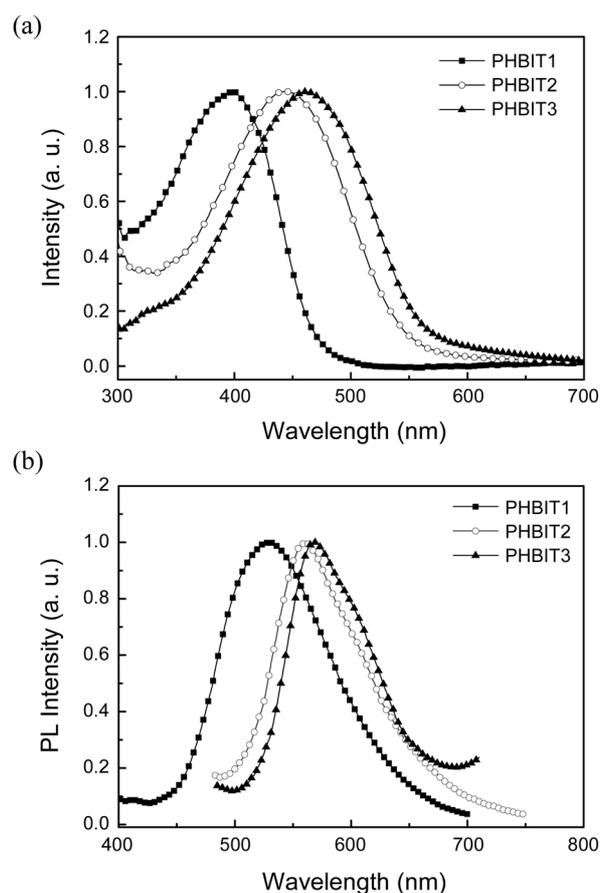


Figure 3. UV-vis absorption (a) and photoluminescence (b) spectra of polymers in thin film.

The DSC analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at a heating rate of 10 °C/min. Thermal gravimetric analysis was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 600 °C. The PHBIT1, PHBIT2 and PHBIT3 showed good thermal stability with onset decomposition temperatures (T_d , 5% weight loss) of 383, 376 and 442 °C, respectively. The PHBIT1, PHBIT2 and PHBIT3 showed good thermal stability with glass transition temperatures (T_g) of 84, 95 and 115 °C. The high thermal stability of the resulting polymers prevents the deformation of the polymer morphology and is important for organic light emitting diode application.

Optical Properties. The UV-vis absorption and photoluminescence (PL) emission spectra of the polymers as solution and thin film are shown in Fig. 2 and Fig. 3. The solution was prepared using chloroform as solvent and the thin film was prepared by spin-coating on quartz plates from the polymer solution in ODCB. The absorption peaks originating from the conjugated backbone of PHBITs appeared at 366 ~ 430 nm, in the solution with chloroform as the solvent. The films of PHBIT1, PHBIT2 and PHBIT3 exhibited absorption spectra with maximum peaks at 398, 444 and 463 nm, respectively, red-shifted around 20 ~ 30 nm as compared to those in solution. The PL emission spectra of

Table 2. Characteristics of the UV-vis absorption and photoluminescence

Polymers	Solution				Film		
	Abs λ_{max} (nm)	PL λ_{max} (nm)	Fwhm ^a of PL	QE _{PL} (%)	Abs λ_{max} (nm)	PL λ_{max} (nm)	Fwhm ^a of PL
PHBIT1	366	500	88	64	398	529	111
PHBIT2	426	546	97	58	444	562	93
PHBIT3	430	561	97	17	463	569	88

^aFull width at half-maximum of PL spectra.

Table 3. Electrochemical potentials and energy levels of the polymers

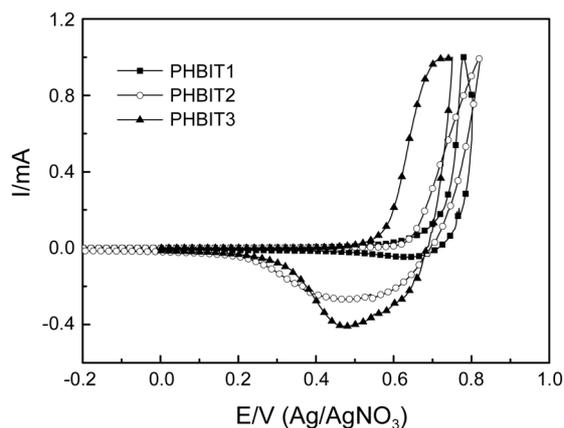
Polymers	Optical band gap ^a (eV)	E_{ox} ^b (V)	HOMO ^c (eV)	LUMO ^d (eV)
PHBIT1	2.64	0.72	-5.52	-2.88
PHBIT2	2.32	0.65	-5.45	-3.13
PHBIT3	2.21	0.58	-5.38	-3.17

^aOptical energy band gap was estimated from the onset wavelength of the optical absorption.

^bOnset oxidation and reduction potential measured by cyclic voltammetry.

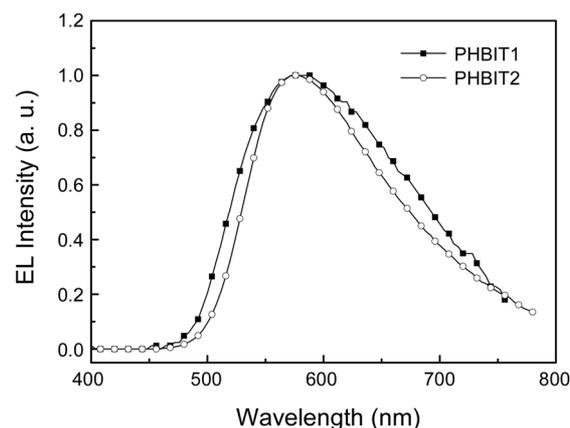
^cCalculated from the oxidation potentials.

^dCalculated from the HOMO energy levels and optical band gap.

**Figure 4.** Electrochemical properties of polymers.

the PHBITs in chloroform solution show maximum peaks at 500 ~ 561 nm. In thin films, maximum peaks of the PHBIT1, PHBIT2 and PHBIT3 appeared at 529, 562 and 569 nm, respectively. The absorption onset wavelengths of the polymers were 469 ~ 560 nm, which correspond to band gaps of 2.21 ~ 2.64 eV. The PL spectra of the films are red-shifted about 25 ~ 40 nm from those of the solutions, caused by the inter-chain interaction of the polymers. The absorption and PL emission spectra exhibit red-shifts with increased number of the thiophene units in the backbone.

Electrochemical Properties. The oxidation potentials derived from the onset values of electrochemical p-dopings and the optical band gaps estimated from the absorption onsets of the polymers are shown in Fig. 4 and summarized in Table 3. HOMO levels were calculated according to the empirical formula ($E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} + 4.80)$ eV). During the anodic scan, the oxidation onset potentials of the polymers are in the range of 0.58 ~ 0.72 V, and exhibited

**Figure 5.** Electroluminescence spectra of devices with the configuration of ITO/PEDOT/PHBITs/Ca:Al.

irreversible p-doping process. HOMO energy levels of PHBIT1, PHBIT2 and PHBIT3 are -5.52, -5.45 and -5.38 eV, respectively. The HOMO energy levels were increased with higher number of the thiophene units, that is, from -5.52 eV in PHBIT1 to -5.38 eV in PHBIT3. The absorption onset wavelengths of the polymers were 469, 535 and 560 nm, which corresponds to band gaps of 2.64, 2.32 and 2.21 eV. The LUMO energy levels were calculated from the values of the band gaps and HOMO energy levels to provide -2.88, -3.13 and -3.17 eV, respectively. The decrease of the LUMO energy levels with increasing number of the thiophene units is attributed to the lower optical band gaps.

Electroluminescent Properties. The investigations of electroluminescence properties of the copolymers were conducted by fabrication of the devices with the configuration of ITO/PEDOT/PHBITs/Ca:Al. The electroluminescence (EL) spectra of the devices are shown in Figure 5. The emission maxima of the PHBIT1 and PHBIT2 appear at around 588 and 576 nm, respectively. The wavelength of the maximum peak in the EL spectrum of PHBIT2 is nearly the same as that in its PL spectra. The EL properties of PHBIT3 could not be measured due to its low solubility. The Commission Internationale d'Enclaireage (1931 CIE) chromaticity coordinates of the EL emissions from PHBIT1 and PHBIT2 were (0.48, 0.50) and (0.50, 0.49), respectively. The current density-voltage (J - V) and luminescence-voltage (L - V) characteristics of the EL devices are shown in Figure 6. The current density and maximum luminescence of PHBIT1 are 220 mA/cm² and 18 cd/m², respectively. The turn-on voltage of PHBIT1 was about 16 V, which is higher than 8V of PHBIT2. The current density and maximum

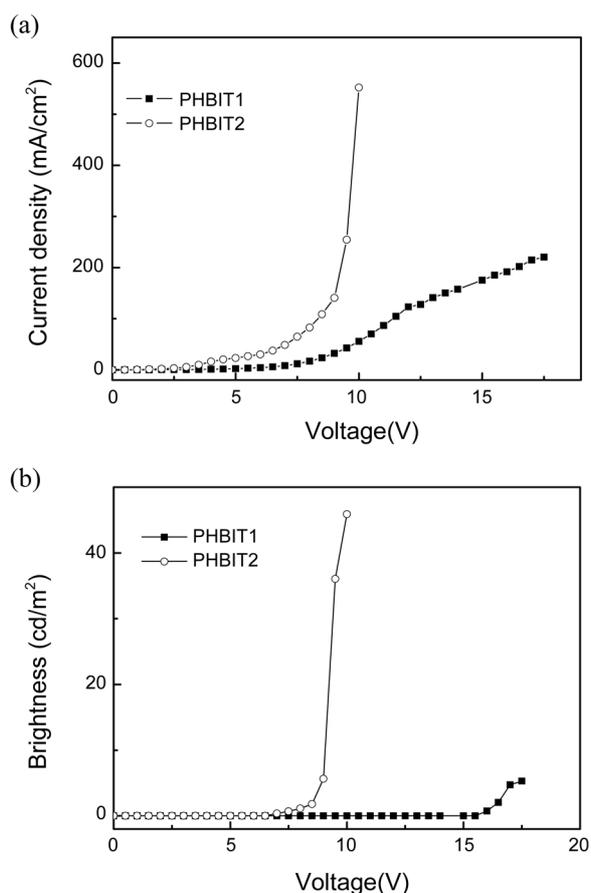


Figure 6. (a) Current density-voltage (J - V) and (b) voltage-luminescence (V - L) characteristics of OLED with the configuration of ITO/PEDOT/PHBITs/Ca:Al.

luminescence of PHBIT2 are 552 mA/cm^2 and 46 cd/m^2 , respectively.

Conclusions

A series of novel copolymers, PHBIT1, PHBIT2 and PHBIT3, containing thiophene units and benzimidazole were synthesized by the Stille polymerization. The film of PHBITs exhibited absorption spectra with maximum peaks at 398, 444 and 463 nm, respectively, red-shifted around 20–30 nm as compared to those in solution. In thin films, maximum peaks of PL spectra of the PHBIT1, PHBIT2 and PHBIT3 appeared at 529, 562 and 569 nm, respectively. The absorption spectra and PL spectra exhibit a red-shift with increased number of the thiophene units in the backbone. The current density and maximum luminescence of PHBIT2 are 552 mA/cm^2 and 46 cd/m^2 , respectively, in the polymer LED with the configuration of ITO/PEDOT/PHBITs/Ca:Al.

Experimental Section

General. All reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-

free atmosphere. ^1H and ^{13}C NMR spectra were recorded with a Varian Gemini-300 (300 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 pre-coated aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) conditions in the Korea Basic Science Institute (Daegu). The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer, while the Oriel InstaSpec IV CCD detection system with xenon lamp was used for the photoluminescence and electroluminescence spectra measurements. The cyclic voltammetry (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 ($\sim 0.05 \text{ cm}^2$) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO₃ electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO₃ reference electrode (calibrated by the FC/FC⁺ redox system) was 4.80 eV below the vacuum level.

EL Device Fabrication and Measurements. For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. The solution of the PEDOT:PSS in aqueous isopropyl alcohol was spin-coated on the surface-treated ITO substrate and dried on a hot plate for 30 min at 110 °C. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting chlorobenzene solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 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 density-voltage (J - V) and luminance-voltage (L - V) characteristics of the devices were measured using a Keithley 2400 Source Measure Unit equipped with a calibrated photo-multiplier tube.

Synthesis of 4,7-Dibromo-2,2-dihexyl-2H-benzimidazole (3). A solution of 3,6-dibromobenzene-1,2-diamine (10 g, 37.65 mmol), 7-tridecanone (10 mL), acetic acid (10 mL), and diethyl ether (200 mL) was heated at 50 °C overnight. After cooling to room temperature, the reaction mixture was treated with water and ethyl acetate. The aqueous phase was extracted with ethyl acetate and combined organic layer was dried with MgSO_4 . After concentration of the organic phase under reduced pressure, the residue was purified by column

chromatography to give 4,7-dibromo-2,2-dihexyl-2,3-dihydro-1*H*-benzimidazole. To a stirred solution of 4,7-dibromo-2,2-dihexyl-2,3-dihydro-1*H*-benzimidazole in 50 mL of tetrahydrofuran (THF) at room temperature was added MnO₂ (10 g). After 3 h, the solid was filtered and washed with THF. The combined organic phase was concentrated under reduced pressure and purified by flash column chromatography to give 4.3 g (26%) of compound **3** as yellow powder. mp 60 °C; 7-Tridecanone was used in this compound. mp 60 °C; ¹H NMR (300 MHz, CDCl₃) δ 0.83 (t, 6H, *J* = 6.87 Hz), 0.92-0.88 (m, 4H), 1.25-1.17 (m, 12H), 2.24-2.18 (m, 4H), 7.20 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 14.26, 22.78, 23.72, 29.62, 31.74, 35.77, 109.92, 118.42, 136.12, 157.87. HRMS (*m/z*, FAB⁺) calcd for C₁₉H₂₈Br₂N₂ 443.0697, found 443.0695.

Synthesis of 2,2-Dihexyl-4,7-di(2-thienyl)-2*H*-benzimidazole (4). To a stirred solution of 4,7-dibromo-2,2-dihexyl-2*H*-benzimidazole (**3**) (4.0 g, 8.9 mmol) and tributyl(2-thienyl)stannane (16.6 g, 44.4 mmol) in 40 mL of THF at room temperature was added dichlorobis(triphenylphosphine)palladium(II) (2 mol %). The reaction mixture was stirred for 12 hr at 80 °C, concentrated under reduced pressure, and purified by flash column chromatography to give 2.5 g (62%) of compound **4** as red solid. mp 81 °C; ¹H NMR (300 MHz, CDCl₃) δ 0.82 (t, 6H, *J* = 6.5 Hz), 1.19-1.09 (m, 16H), 2.17-2.12 (m, 4H), 7.12 (t, 2H, *J* = 4.2 Hz), 7.30 (s, 2H), 7.36 (dd, 2H, *J* = 1.2 Hz, *J* = 5.1 Hz), 8.02 (dd, 2H, *J* = 1.2 Hz, *J* = 3.6 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 14.25, 22.86, 24.33, 29.82, 31.84, 35.77, 110.58, 126.83, 128.07, 128.22, 128.49, 128.61, 139.15, 158.59. HRMS (*m/z*, EI⁺) calcd for C₂₇H₃₄N₂S₂ 450.2163, found 450.2167.

Synthesis of 4,7-Bis(5-bromo-2-thienyl)-2,2-dihexyl-2*H*-benzimidazole (5). To a stirred solution of 2,2-dihexyl-4,7-di(2-thienyl)-2*H*-benzimidazole (**4**) (1.9 g, 4.2 mmol) in THF at room temperature was added *N*-bromosuccinimide (NBS) (1.5 g, 8.6 mmol). After 3h at room temperature, water and ethyl acetate was added. The reaction mixture was washed with 3 × 100 mL of water. The organic phase was concentrated under reduced pressure and purified by flash column chromatography to give 1.8 g (70%) of compound **5** as red solid. mp 116 °C; ¹H NMR (300 MHz, CDCl₃) δ 0.85-0.80 (t, 6H, *J* = 6.6 Hz), 1.19-1.07 (m, 16H), 2.14 (m, 4H), 7.06 (d, 2H, *J* = 3.9 Hz), 7.19 (s, 2H), 7.65 (d, 2H, *J* = 3.9 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 14.25, 22.83, 24.36, 29.79, 31.82, 35.66, 111.08, 115.40, 127.47, 127.77, 127.91, 130.86, 140.26, 158.07. HRMS (*m/z*, EI⁺) calcd for C₂₇H₃₂Br₂N₂S₂ 606.0374, found 606.0369.

General Procedure of Polymerization. Carefully purified dibromo compound (4,7-dibromo-2,2-dihexyl-2*H*-benzimidazole (**3**) or 4,7-bis(5-bromo-2-thienyl)-2,2-dihexyl-2*H*-benzimidazole (**5**)), distannyl compound (2,5-bis(trimethylstannyl)thiophene (**6**) or 5,5'-bis(trimethylstannyl)-2,2'-

bithiophene (**7**)), and (PPh₃)₄Pd(0) (3 mol %) were dissolved in a mixture of toluene and DMF. The mixture was refluxed with vigorous stirring for 2 days under argon atmosphere. After cooling to room temperature, the mixture 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 residual amount of catalyst. The resulting polymer was soluble in THF, CHCl₃, ODCB and toluene.

Acknowledgments. The research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0071669).

References

- Song, S.; Jin, Y.; Kim, S. H.; Shim, J. Y.; Son, S.; Kim, I.; Lee, K.; Suh, H. *J. Polym. Sci. Polym. Chem.* **2009**, *47*, 6540.
- Jin, Y.; Kim, J.; Park, S. H.; Lee, K.; Suh, H. *Bull. Korean Chem. Soc.* **2005**, *26*, 795.
- Jin, Y.; Kim, K.; Song, S.; Kim, J.; Kim, J.; Park, S. H.; Lee, K.; Suh, H. *Bull. Korean Chem. Soc.* **2006**, *27*, 1043.
- Jin, Y.; Kang, J. H.; Song, S.; Park, S. H.; Moon, J.; Woo, H. Y.; Lee, K.; Suh, H. *Bull. Korean Chem. Soc.* **2008**, *29*, 139.
- Tonzola, C. J.; Alam, M. M.; Bean, B. A.; Jenekhe, S. A. *Macromolecules* **2004**, *37*, 3554.
- Cho, S.; Seo, J. H.; Kim, S. H.; Song, S.; Jin, Y.; Lee, K.; Suh, H.; Heeger, A. J. *Appl. Phys. Lett.* **2008**, *93*, 263301.
- Song, S.; Park, S. H.; Jin, Y.; Goo, Y.; Kim, I.; Lee, H.; Lee, K.; Suh, H. *Synth. Met.* **2010**, *160*, 2618.
- Hsieh, B. Y.; Chen, Y. *J. Polym. Sci. Polym. Chem.* **2008**, *46*, 3703.
- Hsieh, B. Y.; Chen, Y. *Macromolecules* **2007**, *40*, 8913.
- 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.
- Liang, Y.; Wu, Y.; Feng, D.; Tsai, S. T.; Son, H. J.; Li, G.; Yu, L. *J. Am. Chem. Soc.* **2009**, *131*, 56.
- Jin, Y.; Kim, J. Y.; Park, S. H.; Kim, J.; Lee, S.; Lee, K.; Suh, H. *Polymer* **2005**, *46*, 12158.
- Song, S.; Jin, Y.; Kim, J.; Park, S. H.; Kim, S. H.; Lee, K.; Suh, H. *Polymer* **2008**, *49*, 5643.
- Jin, Y.; Kim, Y.; Kim, S. H.; Song, S.; Woo, H. Y.; Lee, K.; Suh, H. *Macromolecules* **2008**, *41*, 5548.
- Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108.
- Chung, T. C.; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1984**, *30*, 702.
- Kobayashi, M.; Chen, J.; Chung, T. C.; Moraes, F.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1984**, *9*, 77.
- Tekin, E.; Egbe, D. A. M.; Kranenburg, J. M.; Ulbricht, C.; Rathgeber, S.; Birckner, E.; Rehmann, N.; Meerholz, K.; Schubert, U. S. *Chem. Mater.* **2008**, *20*, 2727.
- Song, S.; Jin, Y.; Park, S. H.; Cho, S.; Kim, I.; Lee, K.; Heeger, A. J.; Suh, H. *J. Mater. Chem.* **2010**, *20*, 6517.
- Song, S.; Park, S. H.; Jin, Y.; Park, J.; Shim, J. Y.; Kim, I.; Lee, H.; Lee, K.; Suh, H. *J. Polym. Sci. Polym. Chem.* **2010**, *48*, 4567.
- Song, S.; Park, S. H.; Jin, Y.; Kim, I.; Lee, K.; Suh, H. *Polymer* **2010**, *51*, 5385.