9282 *Macromolecules* **2002,** *35,* 9282−9288

Exploratory Synthesis and Luminescence Study of the First π-Conjugated Tin-Based Alternating Copolymers for Blue Light-Emitting Diodes at the Very Low Operating Voltage[†]

Nam Seob Baek and Hwan Kyu Kim*

Center for Smart Light-Harvesting Materials and Department of Polymer Science & Engineering, Hannam University, Daejon 306-791, Korea

Eun Hee Chae and Byeang Hyean Kim*

Department of Chemistry and Center for Integrated Molecular Systems, Pohang University of Science and Technology, Pohang 790-784, Korea

Ji-Hoon Lee

Samsung Advanced Institute of Technology, Daejon 103-12, Korea

Received July 22, 2002; Revised Manuscript Received September 25, 2002

ABSTRACT: Tin-based alternating copolymers with a uniform π-conjugated segment were synthesized using the Heck reaction between distyrylstannane monomer and various difunctionalized monomers. The UV−vis absorption maximum peaks of the resulting polymers in chloroform solution and in thin films appeared in the wavelength range of 347−394 nm. Upon photoexcitation with light of wavelength 350 nm, their photoluminescence spectra exhibited an emissive maximum peak around 470−502 nm, corresponding to blue light emission. Multilayered light-emitting diodes with ITO/PEDOT (50 nm)/polymer (80 nm)/Ca (50 nm)/Al (200 nm) composition were fabricated. These LED devices exhibited an emissive maximum peak in the range of 464−472 nm. All of the materials exhibited a very low turn-on voltage of less than 4 V. From cyclic voltammetric studies and optical data, the LUMO level is estimated to be 3.20 eV for SnPhFPV and 2.90 eV for SnPhPVK, and the ionization potentials (HOMO level) were estimated to be 5.90 eV for SnPhFPV and 5.60 eV for SnPhPVK. This lowered LUMO level, in comparison to those of poly(*p*-phenylene) derivatives (such as PPP, ladderlike PPP, and PAF), reduces the energy barrier to electron injection, resulting in a lowering of the operating voltage in the polymeric LED. Compared to devices based on the tin-based polymers alone, devices based on blends between the tin-based polymers and PVK showed improved efficiency of power and luminescence by at least 2−4 times and 3−6 times, respectively. Also for these polymer:PVK blends, the electroluminescence efficiency enhances up to the range of 0.1−0.3 lm/W, and the purity of the emitted blue color improves. These results may be attributed to the intramolecular confinement by diluting the EL polymers with PVK. One of the devices based on a blend system between a tin-based polymer and PVK has a brightness of 2047 cd/m^2 at 11 V with a power efficiency of 0.3 cd/A.

Introduction

In the past few decades, electroluminescent (EL) devices based on π-conjugated polymeric thin layers have attracted much attention because of both their theoretical interest and the potential utility of this technology in a wide variety of applications such as large area flat-panel displays and light-emitting diodes.[1,2] The strong scientific and commercial interest in π-conjugated electroluminescent polymers has been driven by estimates of the huge market potential of large area flat-panel display technology; in addition, small molecule-based full color EL devices are beginning to emerge.[3] In comparison to inorganic EL materials and organic dye molecules,[4,5] EL polymeric materials offer a number of advantages, such as the availability of three primary R/G/B colors through control of the $\pi-\pi^*$ energy gap by manipulation of the molecular structure, fast response times, high quality of display, and ease of device processability with semiconductor technologies.

The realization of full-color displays requires materials that emit light of the three primary colors: red, green, and blue. Although red and green emitters with long lifetime stability and good device performance are already available, there is still strong demand for suitable blue emitters. Intensive research and development has focused on attaining the long-term stability, high efficiency, and bright blue emission at relatively low operating voltages that are the essential requirements of materials used in commercially viable light-emitting diodes. The search for a better polymeric material for use in blue LED devices continues to be a major aim of the research effort in this area. Four main approaches have been demonstrated in the synthesis of suitable blue emitters. The first approach involves developing typical poly(*p*-phenylene) derivatives with large band gaps such as poly(*p*-phenylene)s,[6] poly(alkylfluorene)s,[7] and ladder-type poly(*p*-phenylene)s (LPPP),[8] since not only do these species emit light in the blue region of the visible spectrum but also they offer the possibility of varying the emission wavelength via energy transfer processes. The most important problem with the realization of blue LEDs using these polymers is their tendency to form aggregates/excimers via $\pi-\pi$ interactions in the solid state, resulting in the appearance of an additional emission band in the long wavelength region and a concomitant drop of electroluminescence quantum efficiency. The second approach is

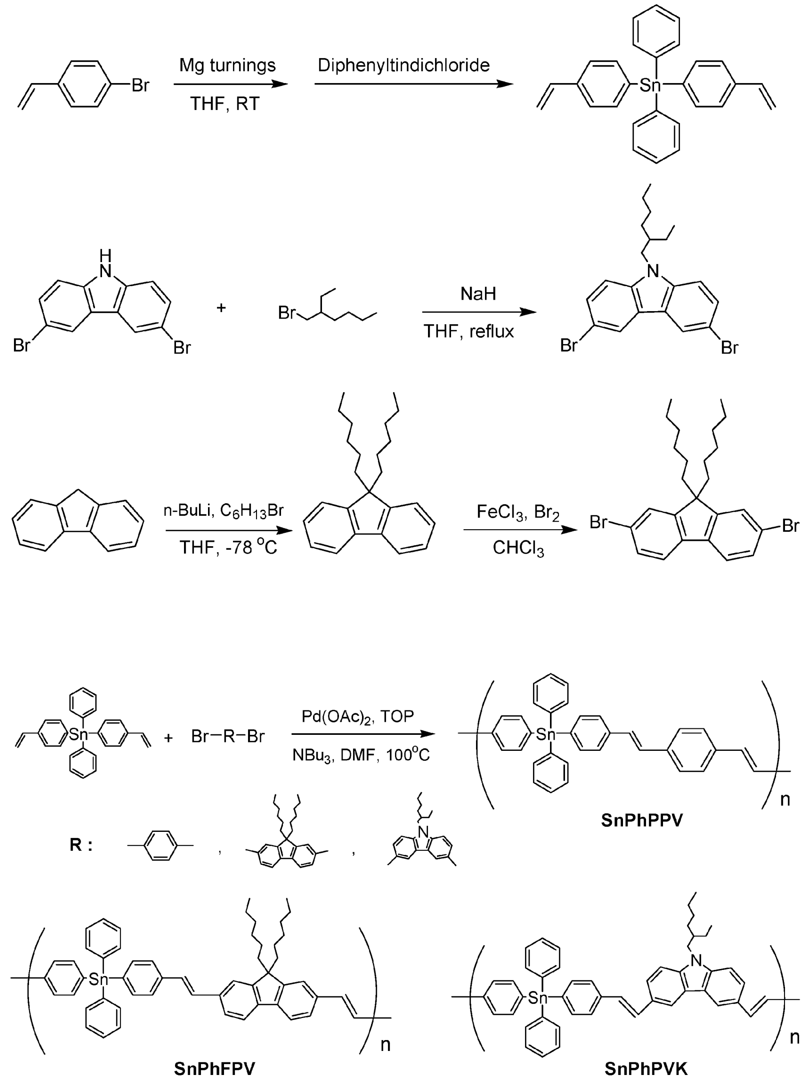
---

[†] This paper is dedicated to Prof. Won-Jei Cho on the occasion of his retirement.

* To whom all correspondence should be addressed. E-mail: hwankkim@mail.hannam.ac.kr or bhkim@postech.ac.kr.

10.1021/ma021165q CCC: $22.00

Scheme 1. Synthesis of Monomers and Tin-Based Alternating Copolymers



to reduce the conjugation length in order to decrease the effective π-conjugation length of the green emitting chromophore. For example, the introduction of *m*-linkages in PPV- or poly(alkylfluorene)-based polymers leads to the interruption of π-conjugation, reducing the π-conjugation length. This reduction tunes the emission color from green to blue.[9]

The third possible approach is to incorporate well-defined conjugated chromophores into π-conjugated EL polymers.[10] In this case, the π-conjugation length of the chromophores can be controlled by introducing flexible nonconjugated segments into the π-conjugated system. This approach has been demonstrated in several instances.[10] However, the incorporation of such flexible segments into a rigid conjugated polymer backbone reduces its stiffness, thus affecting the microscopic molecular order of the polymer and also leading to high turn-on and operating voltages. The fourth approach, developed by our laboratory, is to introduce organosilicon units with aromatic or aliphatic groups into π-conjugated systems, creating so-called silicon-based alternating copolymers, thus limiting the π-conjugation length. This approach has produced blue light-emitting diodes.[11,12] The use of this new class of silicon-based copolymers in light-emitting diodes has the following merits: (1) They offer good processability and easy tuning of EL colors by the incorporation of organosilicon units with aromatic or aliphatic groups on the silicon atoms into the π-conjugated system. (2) Their EL devices exhibit a blue emissive color with a comparably high luminescence efficiency at a low operating voltage of less than 10 V, due to the *d*-orbital participation of silicon atoms and the reduction in the LUMO level.[13] Recently, to balance the hole−electron charges injected and to improve the quantum efficiency, we synthesized novel silicon-based EL copolymers containing oxadiazole and carbazole or fluorene units with various composition ratios.[14] In this paper, similarly, we exploratively develop the first tin-based alternating copolymers with organotin units in the main chain with a blue emissive color. We also fabricate multilayered EL devices using these novel tin-based alternating copolymers, giving a blue emissive color at the very low operating voltage (less than 4 V).

Experimental Section

Materials. 4-Bromostyrene, diphenyltin dichloride, 1,4-dibromobenzene, 2-ethylhexyl bromide, 3,6-dibromocarbazole, fluorene, *n*-butyllithium, ferric chloride, *n*-hexyl bromide, tris(*o*-tolyl)phosphine, and palladium(II) acetate were purchased from Aldrich and used without further purification. All the solvents and other chemicals were used after purification, according to conventional methods, when required.

Monomer Synthesis. The synthesis of monomers was carried out as follows (see Scheme 1).

Distyryldiphenyltin (DSHMT). A mixture of 4-bromostyrene (500 μL, 3.8 mmol) and magnesium turnings (92.4 mg, 3.8 mmol) in dry THF (20 mL) was stirred at 30 °C for 6 h under a nitrogen atmosphere. A solution of diphenyltin dichloride (326.6 mg, 0.95 mmol) in dry THF (10 mL) was added dropwise, and then stirring was continued at the same temperature for 5 h. The reaction mixture was extracted with ethyl acetate and washed with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. Purification of the crude product by column chromatography (silica gel, with hexane/ethyl acetate (15:1) as an eluent) produced a white solid (159 mg, 35%); mp 95−96 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.25 (d, 2H, $J = 10.9$ Hz), 5.77 (d, 2H, $J = 17.6$ Hz), 6.70 (dd, 2H, $J = 17.6$ and 10.9 Hz), 7.24−7.46 (m, 10H), 7.54−7.60 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.5, 138.0, 137.6, 137.4, 137.0, 129.4, 128.9, 126.9, 126.5, 114.7. FT-IR (NaCl, cm^{-1}): 3060, 2987, 2958, 1628, 1588, 1492, 1429, 1300, 1260, 1185, 1159, 1013, 995, 913. HRMS (M^+) Calcd for $C_{28}H_{24}Sn$: 480.0900. Found: 480.0906. Anal. Calcd for $C_{28}H_{24}Sn$: C, 70.18; H, 5.05. Found: C, 69.90; H, 5.32.

3,6-Dibromo-9-(2-ethylhexyl)carbazole and 2,7-dibromo-9,9′-dihexylfluorene were synthesized according to a previously reported procedure,[12] and the chemical structure of these materials was confirmed using FT-IR, ^{1}H NMR, and ^{13}C NMR spectra, elemental analysis, etc.

Polymerization. Novel tin-based copolymers were synthesized according to the well-known Heck reaction,[12,14] as shown in Scheme 1.

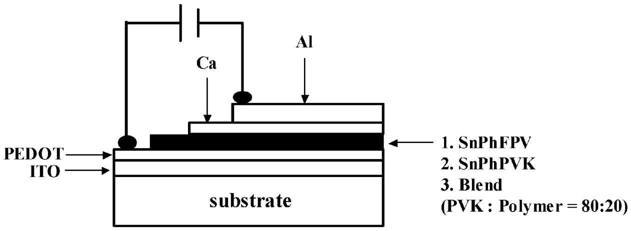
Poly[(9,9′-dihexylfluorene)-*co*-diphenylstannane] (SnPhFPV). 2,7-Dibromo-9,9′-dihexylfluorene (0.822 g, 1.670 mmol) was dissolved in 10 mL of dry DMF at 50 °C under a nitrogen atmosphere. Palladium(II) acetate ($(CH_3CO_2)_2Pd$; 19 mg, 0.083 mmol) and tri(*o*-tolyl)phosphine (TOP: 152 mg, 0.500 mmol) were added, dissolved, and stirred for 1 h. To the resulting solution, distyryldiphenyltin (0.8 g, 1.670 mmol) and tributylamine (4.8 mL, 0.020 mmol) were added and heated overnight at 100 °C with stirring. After 24 h, the reaction mixture was cooled to room temperature and poured into methanol. The resulting precipitate was stirred and washed for 1 h in methanol. The crude polymeric product was filtered off and dissolved in hot chloroform (100 mL). The solution was filtered through a micromembrane filter (0.45 μm) to remove residual catalyst particles and precipitated in methanol. The resulting polymer was dried in a vacuum oven at 50 °C for 1 day, yielding 65% green polymeric product.

Poly[(3,6-*N*-2-ethylhexylcarbazolyl)-*co*-diphenylstannane] (SnPhPVK) and poly[4,4-phenylene-*co*-diphenylstannane] (SnPhPPV) were synthesized by a similar synthetic method.

General Methods. ^{1}H and ^{13}C NMR spectra were recorded with the use of Varian Oxford 300 MHz spectrometers; chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. Chloroform ($CDCl_3$) was the main solvent used for recording NMR spectra. Infrared spectra were measured on neat oil or KBr pellets using a Perkin-Elmer spectrometer. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standards calibration (Water high-pressure GPC assembly model M590 pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, a refractive index detector, solvent: DMF). UV−vis absorption spectra were obtained in chloroform or from thin films on a Perkin-Elmer Lambda 14 spectrophotometer. The photoluminescence spectra were recorded on an Edinburgh FS920 steady-state fluorometer, in which a 450 W xenon arc lamp as excitation source and a S900-R photomultiplier as detector system were installed. Thermal gravimetric analysis and differential scanning calorimetry (DSC) measurements were carried out on a Shimadzu TGA 50 and a TA instruments DSC 2091, respectively. For the measurement of device characteristics, current−voltage ($J-V$) changes were measured using a current/voltage source (Keithley 238) and an optical power meter (Newport 818-SL). Brightness and redox behavior of the polymers were recorded by a PR-650 SpectraScan colorimeter and an EG&G Princeton Applied Research potentiostat model 270, respectively.

Fabrication of Multilayered Light-Emitting Diodes. For the measurement of EL, the polymer light-emitting diodes were constructed as follows. A glass substrate coated with transparent ITO electrode was thoroughly cleaned by successive ultrasonic treatments in acetone and isopropyl alcohol, dried with nitrogen gas, and heated for drying. The surface resistivity of the ITO glass used was ca. 10 ohm/cm^2 (from Samsung Corning. Co.). Before spin-coating the polymers, the surface of the precleaned ITO-coated glass substrate was treated with UV ozone at room temperature for 10 min. For the double-layer devices, a water dispersion of PEDOT [poly-(3,4-ethylenedioxythiophene)] doped with poly(styrenesulfonate) (PSS) (ca. 50 nm, Baytron P CH 8000, Bayer AG, Germany) as a hole-injection/transport layer was spin-coated onto the surface-treated ITO substrate and baked at 110 °C for 5 min. The polymer film of SnPhFPV or SnPhPVK was prepared by spin-casting the polymer solution containing 1% polymer by weight in chlorobenzene. Uniform and pinhole-free films with a thickness of around 80 nm were easily obtained from the resulting polymer solution. The films were baked at 70 °C for 60 min. For all devices, a metal contact (Ca, 50 nm) with an additional encapsulating layer of Al (∼200 nm) was thermally evaporated onto the polymer film through a mask by vacuum evaporation at a pressure below 4×10^{-6} Torr, yielding active areas of 4 mm^2. After the deposition of cathode Ca/Al, the fabricated devices were sealed with cover glass/UV curing agent in a dry box under an N_2 atmosphere. All processes and measurements mentioned above were carried out in air at room temperature.

Devices I−IV were fabricated as follows: device I: ITO/PEDOT/SnPhFPV/Ca/Al; device II: ITO/PEDOT/SnPhPVK/Ca/Al; device III: ITO/PEDOT/ PVK:SnPhFPV (8:2)/Ca/Al; device IV: ITO/PEDOT/ PVK:SnPhPVK (8:2)/Ca/Al.



Cyclic Voltammetry. To examine the redox behavior of the polymers, cyclic voltammetry was utilized. The polymer was coated using the solution-coating method onto a precleaned ITO as a working electrode with area 0.5 cm^2. After coating, the films adhered to the electrode were dried in a vacuum oven for 10 min. The thickness of the polymer film was ca. 3 μm. The measurements were carried out in acetonitrile solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as the supporting electrolyte. The potentials were measured using Ag/Ag$^+$ as reference electrode and Pt wire as counter electrode, respectively. Each measurement was done with an internal standard ferrocene/ferrocenium (FOC), as described in the literature.[15] The resulting potential values were converted to the new revised potential values vs saturated calomel electrode (SCE) by addition of a constant of 0.1588 V. This conversion is based on reduction potentials from the literature.[16] Therefore, the reduction potential of ferrocenium vs SCE is 0.1588 V. The scan rate was 100 mV/s. The HOMO energy values were calculated using the FOC value of −4.8 eV. From optical data and cyclic voltammetric studies, the optical band gaps (E_g) and the ionization potentials (HOMO level) for SnPhFPV and SnPhPVK were evaluated. The optical band gaps are estimated to be 2.68 eV for SnPhFPV and 2.71 eV for SnPhPVK from the analysis of the absorption edge with a plot of ($h\nu$) vs ($\alpha h\nu)^2$, where α, h, and ν are the absorbance, Planck's constant, and the frequency of light, respectively.[17] The electron affinities (LUMO level) of these polymers, approximated by subtracting

Table 1. Polymerization Results and Thermal and Photophysical Properties of Novel Tin-Based Alternating Copolymers

					UV λ_{max} (nm)		PL λ_{max} (nm)	
polymers	yield (%)	M_n[a] ($\times10^{-3}$)	T_g (°C)	T_{ID}[b] (°C)	solution[c]	film[d]	solution[c]	film[d]
SnPhPPV	45	–	153	278	347	–	426	–
SnPhFPV	65	4.6	–	300	394	398	456	470
SnPhPVK	53	2.5	81	314	355	374	453	470

[a] M_n's of the resulting copolymers were determined by gel permeation chromatography using polystyrene standards. In the case of SnPhPPV, its number-average molecular weight could not be measured, because of its poor solubility in THF. [b] Temperature at which initial loss of mass was observed. [c] Concentration = 10^{-4} mol/L in $CHCl_3$. [d] By spin-coating on quartz.

the optical band gap from the ionization potentials (HOMO level) taken from cyclic voltammograms, are 3.20 eV for SnPhFPV and 2.90 eV for SnPhPVK.

Results and Discussion

The Grignard reaction between *p*-styrylmagnesium chloride and diphenyldichlorostannane yields aryl-substituted stannane synthetic products with high conversion, as shown in Scheme 1. The chemical structure of the final monomer was identified by various methods, including FT-IR, ^{1}H NMR and ^{13}C NMR, and elemental analysis. These analyses confirmed that the distyrylstannane monomer had been successfully synthesized. Also, the 3,6-dibromo-9-(2-ethylhexyl)carbazole and 2,7-dibromo-9,9′-dihexylfluorene monomers were synthesized according to a previously reported procedure.[12,14]

We have developed the first tin-based alternating copolymers with organotin units in the main chain, obtaining blue emissive color at the very low operating voltages. Three derivatives of EL copolymers with an organotin unit have been synthesized using the well-known Heck reaction.[12,14,18] The molecular structures of these novel tin-based alternating copolymers are shown in Scheme 1. The polymerization results, as well as the thermal and photophysical properties of these copolymers, are summarized in Table 1. Instead of using the Wittig methodology, the Heck synthetic route for the preparation of these tin-based alternating copolymers was used for the following reasons:[12,14] (1) The Heck polymerization method enables the production of a higher molecular weight polymer than is produced by the Wittig reaction. (2) The Heck route overcomes the problem of low quantum efficiency due to the formation of the triplet state arising from the unreacted aldehyde functional groups in the tin-based copolymers obtained from the Wittig reaction. (3) The Heck reaction directly produces polymers with the desired trans configuration, which is important to optimize the luminescence efficiency and the emissive wavelength. To quantitatively produce polymers in the trans configuration from polymers in the cis configuration using the Wittig reaction requires a further postreaction isomerization step, achieved by heating the crude polymers with a trace of iodine in toluene. The chemical structure and purity of the resulting polymers were investigated by means of FT-IR, ^{1}H NMR, gel permeation chromatography (GPC), and UV–vis absorption and photoluminescence (PL) spectroscopies. In a typical FT-IR spectrum of the tin-based copolymers, vinyl C=C bonds in the monomer produced a vanishingly weak absorption peak at 1600 cm^{-1}. On the other hand, the out-of-plane bending mode of the trans vinylene groups in the polymer produced a new weak, sharp absorption peak at 960 cm^{-1}. This peak indicates that tin-based alternating polymers with trans double bonds have been synthesized. Using ^{1}H NMR studies as the polymerization proceeded, it was observed that the terminal vinyl peaks of the monomers present at 5.25 and 5.77 ppm disappeared and that a new vinylic proton peak in the polymer overlapped with 7.0–7.5 ppm aromatic protons. Also, the broad peaks around 0.2–2.0 ppm were assigned to alkyl protons adjacent to the tin atom and nitrogen atom in a carbazole unit. The broad peak around 4.1 ppm was assigned to the α-methylene protons adjacent to a nitrogen atom in a carbazole unit. These results indicate that relatively high molecular weight polymers were obtained with the disappearance of the terminal vinylic proton peaks of the distyrylstannane monomer.

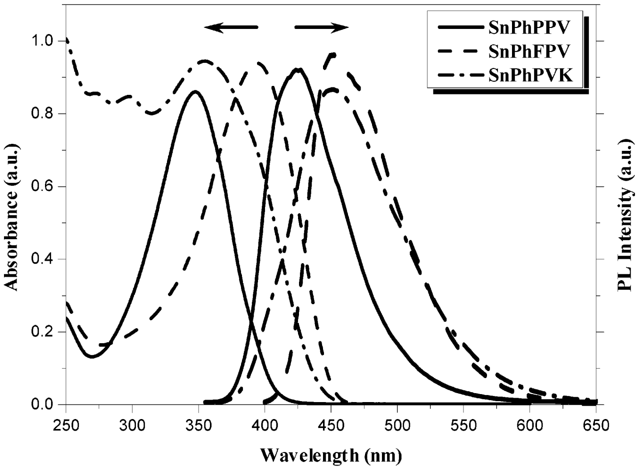


Figure 1. UV–vis absorption and emission spectra of novel tin-based alternating copolymers in $CHCl_3$.

Although rigid π-conjugated polymers are insoluble in common organic solvents, the incorporation of an organotin unit with a long Sn–C bond length (δ_{Sn-C} = 217 pm) into a rigid conjugated polymer backbone reduces its stiffness, due to the lower barrier to rotation about the Sn–C bonds in the polymer backbone, increasing its solubility. The tin-based alternating copolymers are highly soluble in common organic solvents such as THF, $CHCl_3$, CH_2Cl_2, and DMF, and high-quality thin films are obtained by the spin-coating method. The number-average molecular weights (M_n) of the resulting copolymers, as determined by gel permeation chromatography (GPC) using a polystyrene standard, were in the range of 2.5×10^3–4.6×10^3. The thermal behavior of the tin-based copolymers was evaluated by means of DSC and TGA under a nitrogen atmosphere. None of the copolymers exhibited a definite melting point, implying that the tin-based copolymers could be amorphous. This was confirmed by the broadness of their X-ray diffraction patterns. The SnPhPPV and SnPhPVK copolymers have the T_g values of 153 and 81 °C, respectively. The T_g of SnPhPPV is higher than that of SnPhPVK, indicating more rigidity of SnPhPPV. All of the polymers showed good thermal stability up to 278–314 °C; a small amount (less than 1%) of weight

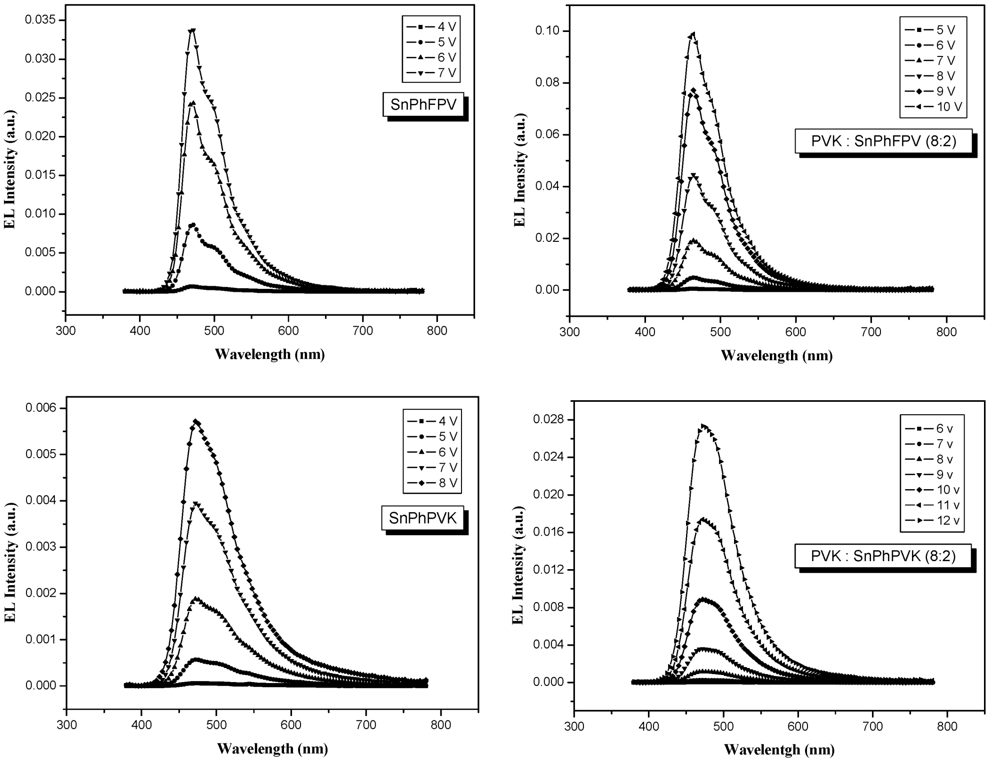


Figure 2. EL spectra of devices I−IV as a function of the applied voltage.

loss began to occur at 300−314 °C under a nitrogen atmosphere.

Figure 1 shows the UV−vis absorption and emission spectra of the copolymers. The UV−vis absorption spectra of the polymers, in chloroform solution and thin films, appear in the wavelength range of 347−394 nm, which is attributed to the $\pi-\pi^*$ transition of the π-conjugated segment. The π-conjugated system is regulated and limited by an organotin unit, resulting in a blue shift. It was also observed that SnPhFPV absorbs at longer wavelength than SnPhPVK. This difference is ascribed to the stronger conjugation properties of fluorene units in comparison to those of carbazole units. Upon photoexcitation with 350 nm, the PL spectra of the copolymers exhibited blue emissive color at around 470−502 nm.

Multilayered light-emitting diodes with ITO/PEDOT (50 nm)/polymer (80 nm)/Ca (50 nm)/Al (200 nm) composition were fabricated and characterized as a function of applied voltage. The electroluminescence spectra for the double-layer devices are shown in Figure 2. Devices based on SnPhFPV and on its blend with PVK emit light at 470 and 464 nm in the blue region, respectively. Also, devices based on SnPhPVK and on its blend with PVK emit light at 472 and 470 nm in the blue region, respectively. Their EL intensity increases with applied voltage. Figure 3 shows the current density as a function of applied voltage for all devices. As can be seen from the $J-V$ curve, all the materials exhibited a very low turn-on voltage of less than 4 V, which is much less than all other known blue EL polymers. Here, the turn-on voltage was defined as the voltage at which the blue EL light can be detected by the eye.

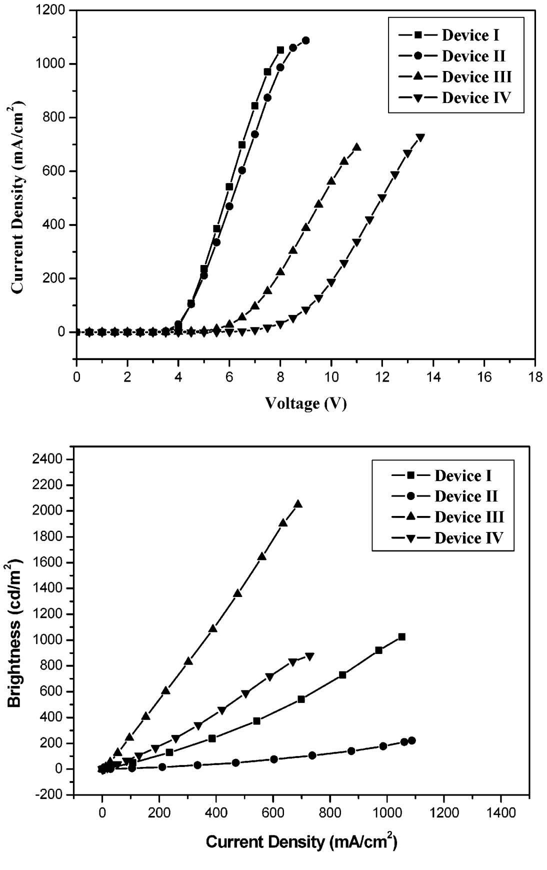


Figure 3. $J-V-L$ characteristics of novel tin-based alternating copolymers.

To understand these results, the electron affinities (LUMO level) and the ionization potentials (HOMO level) of SnPhFPV and SnPhPVK were evaluated from cyclic voltammetric studies and optical data. The LUMO level is estimated to be 3.20 eV for SnPhFPV and 2.90 eV for SnPhPVK, and the ionic potentials (HOMO level) were estimated to be 5.90 eV for SnPhFPV and 5.60 eV for SnPhPVK (see Figure 4). This lowered LUMO level, in comparison to those of poly(p-phenylene) derivatives (such as PPP, ladderlike PPP, and PAF),[6−8,19] reduces

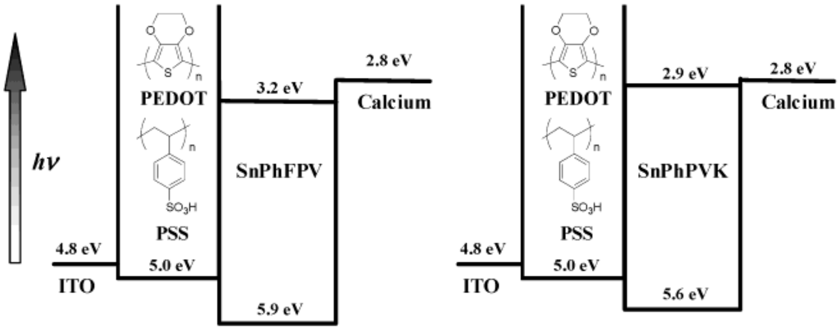


Figure 4. Energy diagram of novel tin-based alternating copolymers.

Table 2. EL Properties and Comparison of CIE 1931 for Devices I−IV Based on Novel Tin-Based Copolymers

polymer system[a]	EL λ_{max} (nm)	brightness (cd/m^2)	operating voltage (V)	current density (mA/cm^2)	power efficiency (cd/A)	lumin efficiency (lm/W)	CIE chart	
							x	*y*
SnPhFPV	470	238	5.5	386	0.062	0.035	0.166	0.289
SnPhPVK	472	222	9	1087	0.020	0.007	0.200	0.306
PVK:SnPhFPV (8:2)	464	242	7	96	0.252	0.113	0.153	0.218
PVK:SnPhPVK (8:2)	470	242	10.5	259	0.094	0.028	0.169	0.286

[a] ITO/PEDOT (50 nm)/polymer (80 nm)/Ca (50 nm)/Al (200 nm).

the energy barrier to electron injection, resulting in a lowering of the operating voltage in the polymeric LED, such as occurs for poly(cyanoterephthalylidene).[20] In comparison to poly(*p*-phenylene) derivatives such as PPP, or ladderlike PPP and PAF, the observed current densities in these materials are relatively high, probably because the tin-based copolymers have higher current characteristics than the poly(*p*-phenylene) derivatives.[6−8] Brightness is shown as a function of current density for devices I−IV in Figure 3. In Table 2, EL properties and comparison of CIE 1931 for devices I−IV based on novel tin-based copolymers, at the brightness range of 220−240 cd/m^2 in the blue color required for the full color display of AM QVGA 320 × 240 (red, 300 cd/m^2; green, 680 cd/m^2; blue, 220 cd/m^2) were summarized. Compared to devices I and II, the power and the electroluminescence efficiency of devices III and IV were higher by at least 2−4 times and 3−6 times, respectively. With these results for all blend systems, the electroluminescence efficiency enhances up to the range of 0.1−0.3 lm/W, and the purity of blue color improves (see Figure SI-2). These results may be attributed to the intramolecular confinement by diluting the EL polymers with PVK. Device III has a brightness of 2047 cd/m^2 at 11 V with a power efficiency of 0.3 cd/A. However, compared to devices I and II, the current density of devices III and IV was much lower by approximately 4 times (see Table 2). It might be explained by the fact that tin-based alternating copolymers have the higher charge-carrier mobility characteristics than PVK, due to their higher degree of conjugation than PVK.

Conclusions

We have exploratively developed the first tin-based alternating copolymers with organotin units in the main chain and used these to obtain LEDs with blue emissive color at the very low operating voltages. Tin-based alternating copolymers with a uniform π-conjugated segment were synthesized using the Heck reaction between distyrylstannane monomer and difunctionalized monomers. The UV−vis absorption maximum peaks of the resulting polymers in chloroform solution and in thin films appeared in the wavelength range of 347−394 nm, and the PL spectra of the copolymers exhibited blue emissive color with the emissive maximum peaks at 470−502 nm. Multilayered light-emitting diodes with ITO/PEDOT (50 nm)/polymer (80 nm)/Ca (50 nm)/Al (200 nm) composition exhibit an emissive peak at 470 nm in the blue region. All of the materials exhibited a very low turn-on voltage of less than 4 V. These results may be due to the reduction of the energy barrier to electron injection arising from their lowered LUMO level, in comparison to those of poly(*p*-phenylene) derivatives (such as PPP, ladderlike PPP, and PAF). In addition, the current density in these LEDs is relatively high, probably because the tin-based copolymers have the higher current characteristics than the poly(*p*-phenylene) derivatives. For systems blending the tin-based polymers and PVK, the efficiency of power and luminescence was improved by at least 2−4 times and 3−6 times, respectively. Also, the electroluminescence efficiency enhances up to the range of 0.1−0.3 lm/W, and the purity of the blue color improves, due to the intramolecular confinement by diluting the EL polymers with PVK. A device based on a blend system between a tin-based polymer and PVK has a brightness of 2047 cd/m^2 at 11 V with a power efficiency of 0.3 cd/A.

Acknowledgment. The authors acknowledge that this research was financially supported by the National Creative Research Initiative Program of the Ministry of Science and Technology of Korea at Hannam University and by the Center for Integrated Molecular Systems at POSTECH.

Supporting Information Available: ^{1}H and ^{13}C NMR data and comparison of CIE 1931 for devices I−IV based on novel tin-based copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) 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. (b) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941. (c) Gustafasson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature (London)* **1992**, *357*, 477.

(2) (a) Berggrenm, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature*

(London) **1994**, *372*, 444. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(3) See http://www.kodak.com/go/oled.

(4) (a) Zhang, C.; Seggern, H. von; Parbaz, K.; Kraabel, B.; Schmidt, H. W.; Heeger, A. J. *Synth. Met.* **1994**, *62*, 35. (b) Fisher, T. A.; Lidzey, D. G.; Pate, M. A.; Weaver, M. S.; Whittaker, D. M.; Skolnick, M. S.; Bradley, D. D. C. *Appl. Phys. Lett.* **1995**, *67*, 1355.

(5) (a) Chang, S. C.; Bharathan, J.; Yang, Y.; Helgeson, R.; Wudl, F.; Ramey, M. B.; Reynolds, J. R. *Appl. Phys. Lett.* **1998**, *73*, 2561. (b) Lupton, J. M.; Samuel, I. D. W.; Beavington, R.; Burn, P. L.; Bassler, H. *Adv. Mater.* **2001**, 258.

(6) (a) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36. (b) Kim, H. K.; Kim, K. D.; Zyung, T. *Mol. Cryst. Liq. Cryst.* **1997**, *295*, 27. (c) Shin, S. H.; Oh, D. J.; Kim, H. K. *Mol. Cryst. Liq. Cryst.* **2000**, *349*, 423.

(7) (a) Fukuda, M.; Sawada, K.; Yosino, K. *J. Polym. Div., Polym. Chem. Ed.* **1993**, *31*, 2465. (b) Grell, M.; Bradley, D. D. C.; Inbasekaran, M.; Woo, E. P. *Adv. Mater.* **1997**, *9*, 798. (c) Setayesh, S.; Marsitzky, D.; Mullen, K. *Macromolecules* **2000**, *33*, 2016.

(8) (a) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Mullen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.

(9) (a) Cho, H. N.; Kim, J. K.; Kim, D. Y.; Kim, C. Y.; Song, N. W.; Kim, D. *Macromolecules* **1999**, *32*, 1476. (b) Liao, L.; Pang, Y.; Dinf, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 7300.

(10) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.

(11) (a) Kim, H. K.; Ryu, M.-K.; Lee, S.-M. *Macromolecules* **1997**, *30*, 1236. (b) Kim, H. K.; Ryu, M.-K.; Kim, K. D.; Lee, S.-M.; Cho, S. W.; Park, J. W. *Macromolecules* **1998**, *31*, 1114.

(12) Jung, S. H.; Kim, H. K.; Kim, S. H.; Jeoung, S. C.; Kim, Y. H.; Kim, D. *Macromolecules* **2000**, *33*, 9277.

(13) Yoshino, Y.; Nichihara, Y.; Ootake, R.; Fujii, A.; Ozaki, M.; Yoshino, K.; Kim, H. K.; Baek, N. S.; Choi, S. K. *J. Appl. Phys.* **2001**, *90*, 6061.

(14) (a) Paik, K. L.; Baek, N. S.; Kim, H. K. *ACS Polym. Prepr.* **2002**, *43* (1), 77. (b) Paik, K. L.; Baek, N. S.; Kim, H. K.; Lee, J. H.; Lee, Y. *Macromolecules* **2002**, *35*, 6782.

(15) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bässer, H.; Porsch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

(16) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 68th ed.; CRC Press: Boca Raton, FL, 1977; pp D151−D158.

(17) Fujii, A.; Ootake, R.; Fujisawa, T.; Ozaki, M.; Ohmori, Y.; Lada, T.; Yoshino, K.; Lu, H.-T.; Chan, H. S. O.; Ng, S.-C. *Appl. Phys. Lett.* **2000**, *77*, 660.

(18) (a) Kim, D. Y.; Cho, H. N.; Kim, C. Y. *Prog. Polym. Sci.* **2000**, *25*, 1089. (b) Peng, Z. H.; Gharavi, A. R.; Yu, L. P. *J. Am. Chem. Soc.* **1997**, *119*, 4622.

(19) Kim, K. D.; Park, J.-S.; Kim, H. K.; Lee T. B.; No, K. T. *Macromolecules* **1998**, *31*, 7267.

(20) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature (London)* **1993**, *365*, 628.

MA021165Q