Synthesis and Optical and Electroluminescent Properties of Novel Conjugated Copolymers Derived from Fluorene and Benzoselenadiazole

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ABSTRACT: A novel series of light-emitting copolymers derived from 9,9-dioctylfluorene (DOF) and 2,1,3-benzoselenadiazole (BSeD) is prepared by means of palladium-catalyzed Suzuki coupling reaction. The feed ratios of DOF to BSeD were 50:50, 85:15, 92:8, and 98:2, respectively. All of the copolymers are soluble in common organic solvents and highly fluorescent in solid state. Devices from such copolymers emit orange-red light with $\lambda_{\max} = 570-600$ nm. The maximal EL emissions of the devices slightly red-shifted gradually with increasing BSeD's contents. The maximal external quantum efficiency of the polymer light-emitting devices (PLED) reaches 1.0%, which indicates that this new seleno-containing EL polymer based on fluorene and benzoselenadiazole is a promising candidate for fabricating PLEDs.

Introduction

The notion that π-conjugated polymeric materials should possess interesting and useful electronic and optical properties is now well established in the scientific literature.[1] Many of these expectations have been realized by the practical demonstration of electronic and optoelectronic devices in which conjugated polymeric materials are responsible for charge transport and/or light generation.[2] Examples include polymer light-emitting diodes (LEDs),[3] photovoltaic devices,[4] and field-effect transistors.[5,6] The wide-ranging applications of electroactive and photoactive conjugated polymers have attracted great interest in the development of functionalized polyacetylenes, polypyrroles, polythiophenes, polyanilines, polyfluorenes, etc.[7] These materials combine the excellent electrical and optical properties of metals or inorganic materials with the advantages of polymeric materials, such as low density, easy processability, and synthetic tunability.[8] The exceptional physical properties of conjugated polymers are mainly related to their π-conjugated backbone which leads to a strong absorption in the UV−visible range and allows the generation of stable and mobile charge carriers to have partial oxidation or reduction.[7,9] The electronic structure of these conjugated polymers is modified by these reversible redox reactions, leading also to new electronic states within the band gap and associated electrochromic properties.[9,10] The electrical and optical activity of these materials relies on the ability of the materials to transport electrical charges: electrons and positive holes through their structures. Such active organic materials, such as oligomers, polymers, or smaller organic compounds, have a commercial advantage over their inorganic counterparts, such as silicon and gallium arsenide. Much of the motivation for studying polymers stems from the potential to tailor desirable optoelectronic properties and processing characteristics by manipulation of the primary chemical structure.[11] Thus, it is easy to raise or lower the HOMO and LUMO levels including conjugation length control, as well as the introduction of electron-donating or -withdrawing groups to the parent chromophore.[12] Regulating the HOMO and LUMO energy levels permits the fine-tuning of charge injection properties. In LED, the HOMO/LUMO energy difference directly controls emission frequency, i.e., emission color.

Light-emitting polymers have revolutionized flat-panel display technology. A large number of light-emitting polymers have been introduced during the last 10 years.[13] Polymers with aromatic or heterocyclic units generally absorb light with wavelengths 300 to 600 nm due to $\pi-\pi^*$ transitions.[14] The color of light, quantum efficiency (QE) of light emission, turn-on voltage, and stability of the devices must be optimized for LEDs to be applicable to commercial light-emitting devices. There have been many attempts to improve the performance of PLEDs. A high quantum efficient, pure, and stable material is essential for commercial LED performance, so many research groups have been developing suitable materials. A series of electroluminescent materials has even been provided as the promising candidates for high-resolution, full color, flat-panel polymeric light-emitting diode (PLED) displays. Among those polymers, polyfluorenes are an important class of electroactive and photoactive material.[15] In the last 4 years, this research field has literally exploded because of polyfluorenes' exceptional optoelectronic properties for applications in light-emitting diodes. Normally, polyfluorene homopolymers have large band gaps and emit blue light. Emission color of polyfluorenes can be tuned in entire visible region by incorporating narrow band gap comonomer into polyfluorene backbone. Most widely used narrow band gap comonomers are a variety of aromatic heterocycles with S and N atoms.[16,17]

Recently, we have reported a series of polyfluorene copolymers prepared by Suzuki coupling of fluorene and sulfur-containing heterocycles.[18] The efficient energy transfer due to exciton trapping on narrow band gap heterocycle sites has been observed. Significant enhancement in the external quantum efficiencies of electroluminescence by exciton confinement in the random copolymers that have regions of different energy gap within a single chain was reported first by Burn et al.[3d]

In this contribution a series of novel copolymers derived from substituted-fluorene and Se-containing

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heterocycles, 2,1,3-benzoselenadiazole synthesized by the palladium-catalyzed Suzuki coupling method, is reported. In contrast to extensively investigated polyfluorene copolymers with S-containing heterocycles—thiophene[9,15] and benzothiadiazole[17,19]—to the best of our knowledge, this is a first report on electroluminescent Se-containing conjugated polymer. Since the Se atom has a much larger size and less electronegativity than the S atom, it would have a more important influence for the heteroatoms on the light-emitting properties of the resulting copolymers. Complete synthetic details and device characterization are presented. The emission properties of Se-containing copolymers are discussed in comparison with its sulfur analogue.

Experimental Section

General Details. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry argon. All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and used as received. All the solvents were further purified before use. ^{1}H and ^{13}C NMR spectra were recorded on a Varinan Inova 500 or Bruker DRX 400 spectrometer operating at 500 and 100 MHz, respectively, and were referred to tetramethylsilane. Analytical GPC was obtained using a Waters GPC 2410 in tetrahydrofuran via a calibration curve of polystyrene standards. Elemental analyses were performed on Vario EL elemental analysis instrument (Elementar Co.). The elemental selenium analysis was recorded on a polarized Zeeman atomic absorption spectrophotometer, Hitachi Co.. UV−visible absorption spectra were recorded on a HP 8453. The PL quantum yields were determined on a Integrating Sphere IS080 with 325 nm excitation from a HeCd laser (Mells Griod). EL efficiency and brightness were carried out with calibrated silicon photodiode. PL and EL spectra were recorded on Instaspec 4 CCD spectrophotometer (Oriel Co.). Cyclic voltammetry was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV/s against calomel reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN).

2,7-Dibromofluorene (1) and 2,7-dibromo-9,9-dioctylfluorene (2) were prepared according to the published procedures.[20]

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (3) was prepared following the modified procedure from 2,7-dibromo-9,9-dioctylfluorene (**2**).[21] The resulting boronic ester was recrystallized from THF and methanol and then further purification by column chromatography (silica gel, 10% ethyl acetate in hexane) to give the product mentioned in the title as a white solid (3.1 g, 46%), mp 128−131 °C. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.80 (d, 2H, fluorene ring), 7.74 (s, 2H, fluorene ring), 7.71 (d, 2H, fluorene ring), 1.99 (m, 4H, H-alkyl), 1.39 (s, 24H, CH_3), 1.22−1.00 (m, 20H, H-alkyl), 0.81 (t, 6H, H-alkyl), 0.56 (m, 4H, H-alkyl). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 150.86, 144.30, 134.04, 129.29, 119.77 (fluorene ring), 84.11 (C-alkyl), 55.57 (C_9, fluorene ring), 40.49, 32.18, 30.33, 29.58, 25.33, 23.98, 22.99, 14.48 (C-alkyl). Anal. Calcd for $C_{41}H_{64}O_4B_2$: C, 76.74; H, 10.04. Found: C, 76.44; H, 9.90.

4,7-Dibromo-2,1,3-benzoselenadiazole (4).[22] Bromine (3.2 g, 0.02 mol) was added to a solution of 2,1,3-benzoselenadiazole (1.83 g, 0.01 mol) and silver sulfate (3.12 g, 0.01 mol) in concentrated sulfuric acid (20 mL). The mixture was shaken at a room temperature for 1.25 h, the precipitate of silver bromide was filtered off, and the filtrate poured into ice−water. The precipitate, from ethyl acetate (500 mL), gave 4,7-dibromo-2,1,3-benzoselenadiazole (2.05 g, 60%) as golden yellow needles, mp 285−287 °C. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.63 (s, 2H, phenylene ring).^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 157.2, 132.1, 116.5. Anal. Calcd for $C_6H_2Br_2N_2Se$: C, 21.1; H, 0.6; Br, 46.9; N, 8.2. Found: C, 21.4; H, 0.9; Br, 46.9; N, 7.8.

General Procedure of Polymerization.[23] Carefully purified 2,7-dibromo-9,9-dioctylfluorene (**2**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**), 4,7-dibromo-2,1,3-benzoselenadiazole (**4**), $(PPh_3)_4Pd^0$ (0.5−2.0 mol %), and several drops of Aliquat 336 were dissolved in a mixture of toluene and aqueous 2 M Na_2CO_3. The solvents were further purified in advance. The solution was refluxed with vigorous stirring for 3 days under argon atmosphere. At the end of polymerization, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene was added to remove bromine end groups and bromobenzene was added as a monofunctional end-capping reagent to remove boronic ester end groups, because boron and bromine units could quench emission and contribute to excimer formation in LED applications.[24] The whole mixture was then poured into methanol. The precipitated material was recovered by filtration through a funnel. The solid material was washed for 24 h using acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF, $CHCl_3$, and toluene. Yields: ∼65−80% respectively.

Poly[2,7-(9,9-dioctylfluorene)-*alt*-4,7-(2,1,3-benzoselenadiazole)] (5a). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (1.00 equiv) and 4,7-dibromo-2,1,3-benzoselenadiazole (**4**) (1.00 equiv) were used in this polymerization. Anal. Found: C, 61.38; H, 6.12; N, 3.63; Se, 10.21.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.04 (2H, fluorene ring), 7.92 (2H, fluorene ring), 7.79 (2H, fluorene ring), 7.61 (2H, benzoselenadiazole ring), 7.26 (benzene ring), 2.12 (4H, H-alkyl), 1.25−1.11 (m, 20H, H-alkyl), 0.95 (t, 6H, H-alkyl), 0.81 (m, 4H, H-alkyl).

^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 160.44 (C-benzoselenadiazole ring), 152.04, 141.22, 137.48, 135.85, 129.04, 128.76, 124.64, 120.23 (C-fluorene ring, C-benzene ring), 55.80 (C_9-fluorene ring), 40.61, 32.23, 30.54, 30.09, 29.68, 24.47, 23.01, 14.47 (C-alkyl).

Poly[2,7-(9,9-dioctylfluorene)-*co*-4,7-(2,1,3-benzoselenadiazole)] (5b). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**2**) (0.35 equiv), and 4,7-dibromo-2,1,3-benzoselenadiazole (**4**) (0.15 equiv) were used in this polymerization. Anal. Found: C, 84.96; H, 9.78; N, 1.10; Se, 3.62.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.03 (2H, fluorene ring), 7.89, 7.85, 7.80, 7.77, 7.68 (fluorene ring), 7.60 (2H, benzoselenadiazole), 7.48, 7.37, 7.27 (benzene ring), 2.12 (4H, H-alkyl), 1.25−1.14 (m, 20H, H-alkyl), 0.94 (t, 6H, H-alkyl), 0.82 (m, 4H, H-alkyl).

^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 160.47 (C-benzoselenadiazole ring), 151.57, 140.35, 126.93, 120.36 (C-fluorene ring, C-benzene ring), 55.35 (C_9-fluorene ring), 40.63, 32.27, 30.60, 30.05, 29.88, 24.52, 22.97, 14.08 (C-alkyl).

Poly[2,7-(9,9-dioctylfluorene)-*co*-4,7-(2,1,3-benzoselenadiazole)] (5c). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**2**) (0.42 equiv), and 4,7-dibromo-2,1,3-benzoselenadiazole (**4**) (0.08 equiv) were used in this polymerization. Anal. Found: C, 83.99; H, 9.84; N, 0.43; Se, 1.35.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.06 (2H, fluorene ring), 7.94, 7.87, 7.80, 7.78, 7.72 (fluorene ring), 7.65 (2H, benzoselenadiazole), 7.51, 7.40, 7.28 (benzene ring), 2.16 (4H, H-alkyl), 1.29−1.17 (m, 20H, H-alkyl), 0.96 (t, 6H, H-alkyl), 0.85 (m, 4H, H-alkyl).

^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 160.48 (C-benzoselenadiazole ring), 152.23, 140.94, 140.44, 126.58, 121.92, 120.38 (C-fluorene ring, C-benzene ring), 55.76 (C_9-fluorene ring), 40.79, 32.19, 30.44, 30.11, 29.61, 24.34, 22.99, 14.44 (C-alkyl).

Poly[2,7-(9,9-dioctylfluorene)-*co*-4,7-(2,1,3-benzoselenadiazole)] (5d). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**2**) (0.48 equiv), and 4,7-dibromo-2,1,3-benzoselenadiazole (**4**) (0.02 equiv) were used in this polymerization. Anal. Found: C, 87.97; H, 10.14; N, <0.3; Se, 0.46.

^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.02 (2H, fluorene ring), 7.85, 7.70, 7.68 (fluorene ring), 7.59 (2H, benzoselenadiazole), 7.49, 7.37, 7.26 (benzene ring), 2.13 (4H, H-alkyl),

Scheme 1. Synthetic Route of the Copolymers

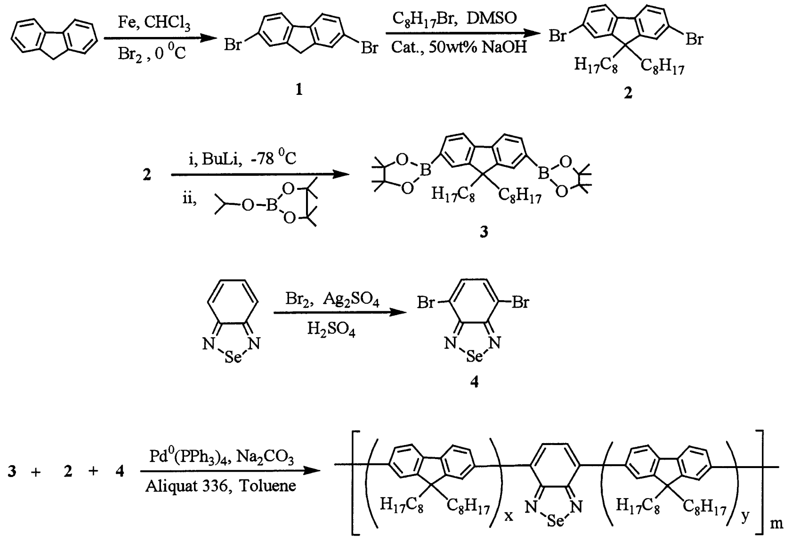

Table 1. Molecular Weights of the Copolymers and Copolymer Composition Determined by Elemental Analysis

			DOF/ BSeD		
copolymers	M_n ($\times 10^3$)[a]	M_w/M_n	in the feed composition	in the copolymers[b]	in the copolymers[c]
DOF 50/ BSeD 50 (**5a**)	16	2.04	50:50	60:40	53.5:46.5
DOF 85/ BSeD 15 (**5b**)	32	3.15	85:15	84:16	86:14
DOF 92/ BSeD 8 (**5c**)	28	2.78	92:8	93.5:6.5	94:6
DOF 98/ BSeD 2 (**5d**)	26	2.56	98:2	97.8:2.2	

[a] Measured by gel permeation chromatography (GPC) referenced to polystyrene standards. [b] Calculated based on elemental analysis of Se and carbon (Se was measured on a polarized Zeeman atomic absorption spectrophotometer). [c] Calculated based on elemental analysis of N and carbon content (N was measured on a Vario EL elemental analysis instrument (Elementar Co.)).

1.25–1.14 (m, 20H, H-alkyl), 0.83 (t, 6H, H-alkyl), 0.69 (m, 4H, H-alkyl).

^{13}C NMR (100 MHz, CDCl$_3$), δ (ppm): 160.42 (C-benzoselenadiazole), 152.22, 140.92, 140.43, 126.56, 121.91, 120.34 (C-fluorene ring, C-benzene ring), 55.75 (C$_9$-fluorene ring), 40.78, 32.20, 30.43, 30.09, 29.60, 24.32, 23.00, 14.43 (C-alkyl).

Results and Discussion

Synthesis and Chemical Characterization. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene was prepared by routine method.[21] 4,7-Dibromo-2,1,3-benzoselenadiazole was prepared by bromination of benzoselenadiazole.[22] Following the synthetic route in Scheme 1, conjugated copolymers derived from 2,7-dibromo-9,9-dioctylfluorene (**2**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**), and 4,7-dibromo-2,1,3-benzoselenadiazole (**4**) have been prepared by using palladium-catalyzed Suzuki coupling methods. The utilization of 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**3**) simplified their purification by column chromatography combined with the advantage of the presence of a protecting group on the boronic acid moieties. The comonomer ratios of DOF to BSeD are 50:50, 85:15, 92:8, and 98:2, and the corresponding copolymers are named **5a**–**d**, respectively. The intent to adjust the starting monomer ratios is to investigate the effects of various copolymer compositions on the LEDs' electrical and optical properties. When the concentration of BSeD in the copolymers is less than 50%, as the characteristic of Suzuki coupling reaction, the obtained polymers **5b**–**d** have random copolymers of a kind of special structure that consists of the fluorene segments of different lengths separated by a single BSeD unit from both sides of each segments. In comparison, **5a** has a regular alternating A–B structure. The resulting copolymers are completely soluble in CHCl$_3$, THF, and toluene. On the basis of GPC, the number-average molecular weights of these polymers are relatively high, from 16 000 to 32 000 with a polydispersity index (M_w/M_n) from 2.0 to 3.15, which is consistent with a polycondensation reaction. The selenium contents of these polymers measured by atomic absorption spectroscopy are close to the feed ratios (Table 1).

The starting monomer ratios have been adjusted in order to investigate the effect of copolymer composition on the physical and optical properties. The actual ratio of DOF to BSeD in the copolymer can be estimated by elemental analysis. The calculated DOF/BSeD ratio from elemental analysis of Se or N and C is listed in Table 1, and it is very close to the feed ratio. A slightly different result for the alternating copolymers (DOF/BSeD50) calculated from Se content measured by atomic absorption spectra might be due to low sensitivity for samples with high Se content. The value calculated from N content gives a more reasonable result. Incorporating of BSeD into the polyfluorene main chain is also consistent with the absorption spectra, where the intensity of the 470 nm peak corresponding to BSeD absorption (shown below) increases with increasing BSeD content in the copolymers.

IR spectra of copolymers were examined and consistent with designed structure. The ^{1}H NMR (500 MHz, CDCl$_3$) spectra of the copolymers show that ca. 8.05–7.70 ppm represent the H atoms on the fluorene ring, 2.12–0.70 ppm are for the H atoms at the substituted octyl on C$_9$ position of the fluorene ring, and about 7.60

Table 2. UV–Vis Absorption, Electrochemical, and Photoluminescent Properties of the Copolymers in Solid State Films

		optical band gap/eV						photoluminescence	
copolymers	λ(abs)$_{max}$/nm	PFO[a]	BSeD[b]	E_{ox}/V	E_{red}/V	HOMO/eV	LUMO/eV	λ_{max}/nm	QE/%
DOF50/BSeD50 (**5a**)	342, 487	3.18	2.18	1.39	−2.26	−5.79	−2.14	595	16
DOF85/BSeD15 (**5b**)	375, 469	2.88	2.32	1.30	−2.20	−5.70	−2.20	579	52
DOF92/BSeD8 (**5c**)	374, 468	2.88	2.30	1.31	−2.19	−5.71	−2.21	563	21
DOF98/BSeD2 (**5d**)	382	2.88		1.28	−2.18	−5.68	−2.22	568	27

[a] Estimated from the onset of absorption peak responsible for fluorene segment. [b] Estimated from the onset of absorption peak responsible for BSeD unit.

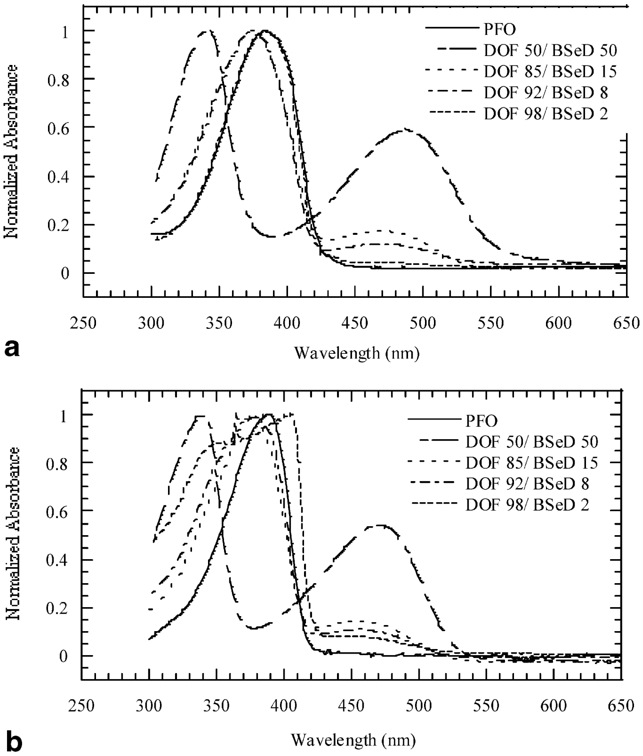

Figure 1. (a) UV–visible absorption spectra for the copolymers in the solid-state films. (b) UV–visible absorption spectra for the copolymers in the $CHCl_3$ solution.

ppm represents the H atoms on the benzoselenadiazole ring. From the ^{13}C NMR (100 MHz, $CDCl_3$) spectra of the copolymers, about 160 ppm is the C atoms of benzoselenadiazole ring, 152–120 ppm represent C atoms on the fluorene and benzoselenadiazole rings, ca. 55 ppm is C_9 on fluorene ring, and 40–14 ppm are C atoms at the substituted octyl on C_9 position of the fluorene ring. ^{1}H NMR and ^{13}C NMR show that the copolymers are right on target molecular structures containing alkyl-substituted fluorene and benzoselenadiazole.

Optical Properties and Electrochemical Characteristics. The UV–visible absorption properties of the conjugated polymers based on fluorene and benzoselenadiazole are presented in Table 2. The absorption spectra of PFO–BSeD copolymers in the solid film show two absorption peaks at ca. 380 and 470 nm. The 380 nm peak is due to the PFO segment, and the 470 nm peak is due to the BSeD unit (Figure 1a). A long wavelength peak for 2% BSeD copolymer is not apparent in solid-state film, but it appears clear in the chloroform solution spectra (Figure 1b). With increasing BSeD concentration in the copolymers, the intensity of the long wavelength peak increases. For the alternating copolymer, the absorption feature at 380 nm due to the PFO segment disappeared completely. This indicates that a new band structure forms due to band alternation. Two distinguished absorption features for the copolymers demonstrate that the electronic configuration of both components, DOF and BSeD, in the copolymers are not mixed.

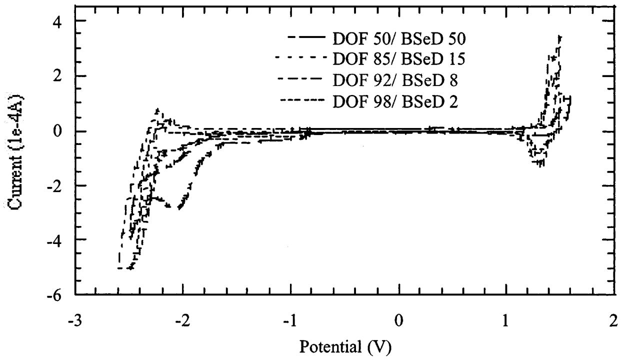

Figure 2. Cyclic voltammograms of the copolymers films on glassy carbon in 0.1 mol/L Bu_4NPF_6, CH_3CN solution.

The electrochemical behavior of the copolymers was investigated by cyclic voltammetry (CV). The positions of CV figures of the copolymers are very similar except alternating copolymer (DOF/BSeD50) (Figure 2). Table 2 summarizes oxidation and reduction potentials derived from the onset of oxidation waves in the cyclic voltammograms of the copolymers. The onset of oxidation process is almost constant at about 1.28–1.32 V for the copolymers except alternating copolymer. This peak is attributed to p-doping of DOF segments. The onset of n-doping waves of DOF segments occurs at −(2.17–2.20) V except for the alternating copolymer. The oxidation and reduction potentials of the alternating copolymer, $E_{ox} = 1.39$ V and $E_{red} = -2.14$ V, are very close to the data reported for polyfluorene homopolymer, $E_{ox} = 1.4$ V and $I_p = 5.8$ eV.[25] Unfortunately, we were unable to record the p- and n-doping of the BSeD unit after many trials. HOMO and LUMO levels calculated according to an empirical formula ($E_{HOMO} = -e(E_{ox} + 4.4)$ eV and $E_{LUMO} = -e(E_{red} + 4.4)$ eV)[26] are also listed in Table 2. The oxidation and reduction processes in the cyclic voltammograms and the similarity of HOMO and LUMO levels values for DOF segment in the copolymers and for polyfluorene homopolymer show that the electronic configuration of both DOF segments are not changed significantly by incorporation of BSeD unit in the copolymers. This is quite consistent with the two separated absorption peaks observed in the UV–visible spectra (Figure 1).

Photoluminescence Properties. The photoluminescent (PL) spectra of the copolymers by excitation of 325 nm line of the HeCd laser in thin film are completely different from those of polyfluorene homopolymer (Figure 3). Polyfluorene homopolymer has double peak at about 426 and 439 nm due to the fluorene segment with a small shoulder at around 490 nm due to vibronic

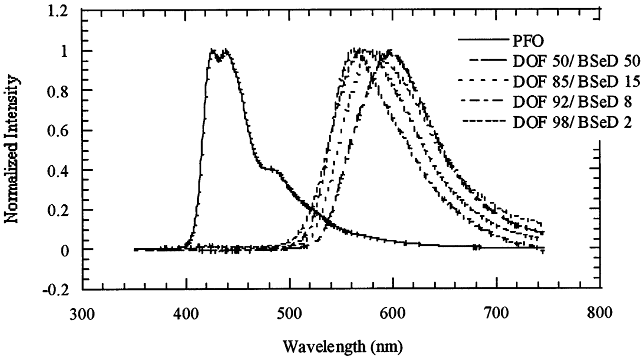

Figure 3. PL spectra for the copolymers in the thin films.

structure (Figure 3, solid line). Once the BSeD unit is incorporated into the polyfluorene main chain, the PL emission was changed dramatically; that is, the PL emission due to the fluorene segment completely disappeared (Figure 3, dotted line). PL emission consists exclusively of BSeD unit emission at around 568−595 nm depending on the BSeD content even though the BSeD concentration is only 2% in the copolymer (Figure 3). The shapes of the PL spectra for copolymers with different BSeD content are very similar, and the PL peaks are significantly red-shifted with increasing BSeD content in the copolymers, from $\lambda_{\max} = 568$ nm for the copolymer with 2% BSeD content to 595 nm for the alternating copolymer. Since no such large red shift was observed for absorption spectra of corresponding copolymers, the significant red-shift in PL emission indicates that the Stokes shift was increasing with the increase in BSeD content in the copolymers. This fact implies that the chain became more rigid with increasing BSeD content in the copolymers. Similar increases in the Stokes shift between the absorption and emission spectra were reported for MEH−PPV at lower temperatures, and it was interpreted as the increase in the conjugation length at lowering the temperature.[27]

The complete disappearance of fluorene emission and the appearance of new emissions due to the BSeD unit indicate that the BSeD unit serves as a powerful trap in the copolymer chain. As we reported previously for polyfluorene copolymers prepared by Suzuki coupling of fluorene and narrow band gap sulfur-containing heterocycles, the trapping mechanism is especially favorable, since both HOMO and LUMO levels of the narrow band gap unit are located within the band gap of the host segment.[18] Although we were unable to detect the oxidation wave due to the BSeD unit in the DOF−BSeD copolymers; however, two distinct oxidation peaks (1.24 V for the PFO segment, 0.97 V for the BTDZ unit) were recorded in cyclic voltammograms of sulfur analogue, poly(fluorene-*co*-benzothiadiazole) (PFO−BTDZ). This fact indicates unambiguously that both HOMO and LUMO levels of BTDZ are located within the band gap of the polyfluorene host. Considering the similarity in absorption, PL, and EL spectra of both types of copolymers and also that BSeD has a more narrow gap than BTDZ, we could assume that both HOMO and LUMO levels of BSeD unit are located within the band gap of the PFO host segment. In results, the excitation energy on the fluorene segments is transferred to the BSeD unit with very high efficiency. Excitons are confined and recombined in BSeD unit isolated from both sides by fluorene segment and emit orange-red light corresponding to BSeD emission. Energy transfer from fluorene segment to BSeD unit may happen via intra- or intermolecular mechanism. To elucidate the relative role of intrachain and interchain energy transfer, we investigated the concentration dependence of PL spectra of DOF−BSeD copolymers in the solution. In Figure 4a, PL spectra of the DOF−BSeD copolymers in very dilute concentration of 1×10^{-5} mol/L (sufficiently low to avoid a strong interchain interaction between polymer chains in the solution) were taken with 325 nm excitation from a HeCd laser. As can be seen from Figure 4a, for copolymers with high BSeD content, DOF/BSeD15 and DOF/BSeD50, polymer solutions emit exclusively BSeD emission. This indicates complete energy transfer from the fluorene segment to BSeD unit when an intramolecular trapping mechanism takes place. However, for DOF/BSeD2 and DOF/BSeD8, along with the main emission peak in the red region, a small emission peak with low intensity due to the fluorene segment can be observed in the PL spectra. Compared with the PL spectra in solid state films (Figure 3) where fluorene emission is completely disappeared, the fact unambiguously indicates the energy transfer in such concentrations is incomplete for copolymers with low BSeD content (≤8%). We also note that, in the case of DOF 98/BSeD2 copolymer with a number-average molecular weight of 2.6×10^4 (Table 1), statistically, only two out of three copolymer chains contain one BSeD unit; the interchain energy transfer must take place in the solid state film in order to depress PL emission from fluorene segment completely, though the intramolecular trapping mechanism is obviously dominant. Figure 4b shows the PL spectra in chloroform solution in different concentration for DOF98/BSeD2 where the DOF emission disappears at a concentration of $\geq 1 \times 10^{-4}$ mol/L (Figure 4b). This threshold concentration decreases with increasing BSeD content, being 1×10^{-6} mol/L for DOF 85/BSeD15 (Table 3). Table 3 lists threshold concentrations in solution for each copolymer where emission from DOF segment is completely depressed. A very low threshold

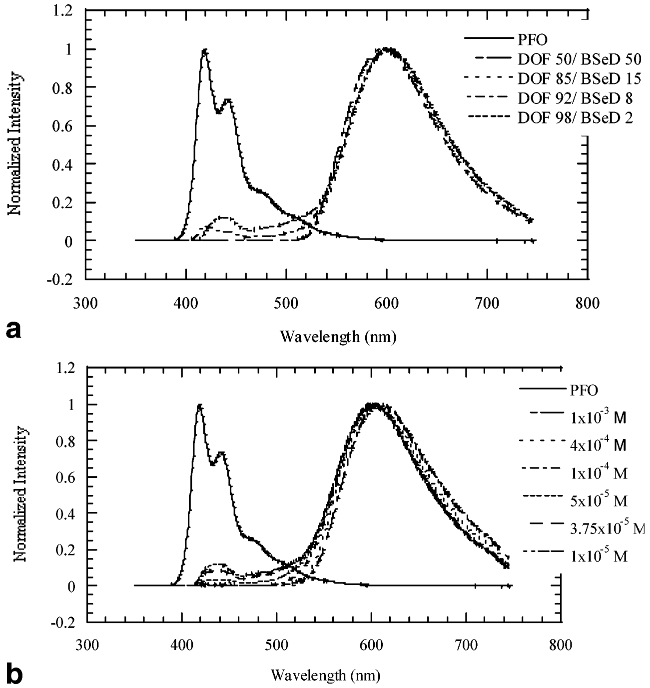

Figure 4. (a) PL spectra of the copolymers in the chloroform solution at the concentration of 1×10^{-5} mol/L. (b) PL spectra for the copolymer **5d** (DOF 98/BSeD 2) in the chloroform solution in different concentration.

Table 3. Threshold Concentration of Copolymers at Which Fluorescence of Fluorene Segment Just Appears

copolymers	threshold concentration/(mol/L)
DOF 50/ BSeD 50 (**5a**)	1×10^{-8}
DOF 85/ BSeD 15 (**5b**)	1×10^{-6}
DOF 92/ BSeD 8 (**5c**)	1×10^{-5}
DOF 98/ BSeD 2 (**5d**)	5×10^{-5}

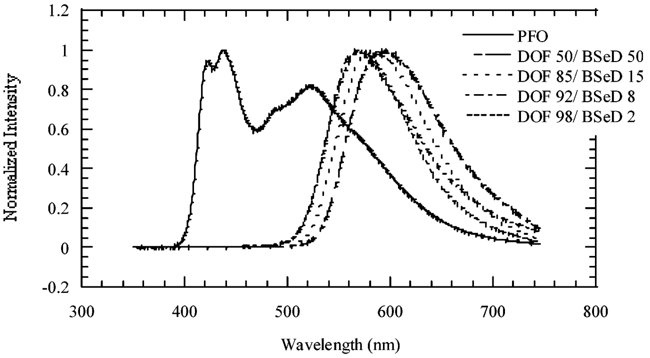

Figure 5. EL spectra for the copolymers in the films.

concentration for completed depression of fluorene host emission seems to suggest that the intramolecular trapping mechanism plays a major role in such copolymers in the solution. However, the increase in the threshold concentration with decreasing the BSeD content in the copolymer (Table 3) indicates that the interchain energy transfer also plays a certain role in the energy transfer from the excited state of the fluorene segment to the BSeD unit. Such a copolymer system serves as an ideal prototype for investigation of intra- and interchain polymer interaction in the polymer solution.

It is worthwhile to also note that, in contrast to PL emission in the solid state (Figure 3), PL peaks almost do not change with the BSeD content in the copolymer solution (Figure 4a) and peak emission always appears at around 600 nm. As mentioned above, PL spectra in the solid film are red-shifting with increasing BSeD content (Figure 3). This fact seems to support the above argument about the possible explanation of red shift of PL emissions in the solid state, since chain rigidity of the DOF−BSeD copolymer could not change significantly in the dilute solution; therefore, the Stokes shift does not change in the solution.

Listed in Table 2 are the PL efficiency and the maximum emission wavelength of the copolymers in thin films. The copolymer containing 15% BSeD (**5b)** has the maximal efficiency of 52%. The efficiency of the alternating polymer, **5a**, decreases to 16%.

Electroluminescent Properties. A double-layer device was fabricated in the configuration, ITO/PEDT (or PVK)/DOF−BSeD/Ba/Al. The EL spectra from such a device are presented in Figure 5, EL spectra of device with polyfluorene homopolymer also shown in Figure 5 for comparison. In the case of PL spectra in the solid film (Figure 3), EL emission due to the fluorene segment was completely disappeared even though the BSeD concentration is only 2% in the copolymer. Similar to PL emission in the solid state, EL emission consists exclusively of BSeD unit emission with an emission peak at around 573−594 nm depending on the BSeD content. EL peaks are also red-shifted with increasing narrow band gap content as in PL emission. Table 4 lists emission maximum and chromaticity coordinate for devices from each copolymer. It is noted that excimer emission appearing in devices from polyfluorene homopolymer (which is absent in the PL spectra of PF homopolymer (Figure 3)) was quenched completely in the copolymers, starting from a BSeD loading as low as 2%. Incorporation of only 2% BSeD units into copolymers chain depresses completely both the fluorene host emission ($\lambda_{\max} = 420$ nm) and the wide excimer emission ($\lambda_{\max} = 540$ nm) indicates that intrachain energy trapping process (from fluorene segment to BSeD unit) must be very fast and intrachain energy trapping should be more efficient than interchain interaction between fluorene segments. This indicates again that intramolecular energy transfer is important in the devices made from such copolymers.

For the copolymers mentioned above, energy transfer probably occurs mainly within the polymer chain via a intramolecular trapping mechanism. Similar behavior was reported by us for the copolymer of fluorene with 4,7-dithien-2-yl-2,1,3-benzothiadiazole[18] and poly(3,6-carbazole) with benzothiadiazole synthesized by Suzuki coupling.[28] It indicates that intramolecular energy trapping in such copolymers is a very quick and efficient process, where an individual narrow band gap unit separated by random fluorene segment from both sides serves as a efficient trap for generated excitons on the fluorene host. As a result, the generated excitons are efficiently confined and recombined on BSeD sites, and copolymers emit exclusively emission of narrow band gap component.

Preliminary device data are promising. The external EL quantum efficiency (QE) reached 1.0% for copolymer of DOF/BSeD15 with peak EL emission at ca. 580 nm for devices with PVK as hole transport layer (Table 4). When PEDT−PSS was used, the device efficiencies are much lower. The results indicate that a relatively high energy barrier exists for hole injection in this case. This is quite consistent with HOMO levels of PFO−BSeD copolymers (5.7−5.8 eV, Table 2) and work function of hole transport layers: PVK, 5.8 eV, and PEDT−PSS, 4.8−5.0 eV.[29] Efforts at further improvement of the PLEDs' efficiency with DOF/BSeD copolymers are in progress and will be reported on elsewhere.

We have synthesized a PFO copolymer with benzothiadiazole (BTDZ), a sulfur analogue of benzoselenadiazole (BSeD) in a different composition. In Figure 6,

Table 4. Device Performances of the Copolymers

		device performances[a]						
copolymers	hole transport layer	$\lambda_{\mathrm{Elsmax}}$/nm	*V*/V	*I*/mA cm^{-2}	cd/m^{-2}	QE/%	chromaticity (*x*)	coordinate (*y*)
DOF 50/ BSeD 50 (**5a**)	PVK	600	13.9	5	147	0.42	0.706	0.292
	PEDT	594	11.0	5	16	0.05	0.705	0.295
DOF 85/ BSeD 15 (**5b**)	PVK	582	13.7	5	345	1.0	0.698	0.300
	PEDT	580	9.8	5	156	0.44	0.696	0.304
DOF 98/ BSeD 2 (**5d**)	PVK	574	29.0	5	278	0.81	0.689	0.314
	PEDT	573	22.1	5	148	0.43	0.683	0.316

[a] Device structure: ITO/hole transport layer/PFO−BSeD/Ba/Al; active area 0.15 cm^2.

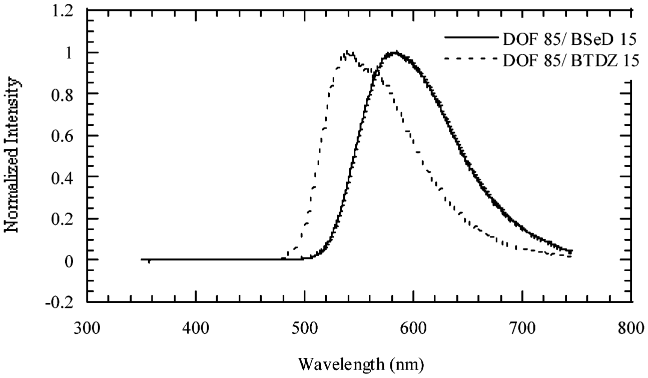

Figure 6. EL spectra for DOF 85/BSeD 15 and DOF 85/BTDZ 15 in thin films.

Table 5. Device Performances of the Copolymers Comparison between BSeD and its Sulfur Analogue BTDZ[a]

	photoluminescence		electroluminescence	
copolymers	λ_{max}/nm	Q_{max}/%	λ_{max}/nm	QE_{ext}/%
DOF 85/ BSeD 15 (**5b**)	579	52	582	1.0
DOF 85/ BTDZ 15	538	60	530	1.5

[a] Device structure: ITO/pvk/copolymer/Ba/Al; active area 0.15 cm^2.

EL spectra for copolymers DOF 85/BSeD 15 and DOF 85/BTDZ 15 are compared. The copolymer with 15% BSeD content emits light at 580 nm, while its sulfur analogue, DOF 85/BTDZ 15, emits at 530 nm. EL emission peaks and efficiencies for devices from these two copolymers are compared in Table 5. A similar red shift in comparison with the S-analogue was observed for PL spectra of Se-containing polymers in different compositions. Significant red-shifts in PL and EL spectra of Se-containing copolymers vs its S-analogue can be expected from the nature of aromatic Se-containing heterocycles. Since the Se atom has less electronegativity (2.55[30]) than the S atom (2.58[30]), electrons in Se containing heterocycles tend to be less concentrated in the Se atom than in the S atom. UV absorption spectra show that the $\pi-\pi^*$ transition of a Se heterocycle (benzoselenophene) undergoes a bathochromic shift around 20 nm longer than that of its S analogue (benzothiophene).[31] It should be also noted that the larger atomic size of Se atom (117 pm[30]) than S atom (104 pm[30]) could increase interaction between BSeD units in different copolymer chains. Thus, interaction between BSeD units in neighboring chains could contribute to the red shift of the Se-containing copolymer too. It will be interesting to use these two types of copolymers (Se- and S-containing copolymers) for the investigation of intra- and interchain interaction in the light-emitting polymers. A further comparative study of these two types of copolymers will be continued.

Conclusion

A novel EL polymer, poly(9,9-dioctylfluorene-*co*-benzoselenadiazole), was successfully synthesized. The efficient energy transfer due to exciton confinement on narrow band gap BSeD sites has been observed. Emission from the DOF segment was completely depressed even at very low BSeD content (2%) due to efficient confinement of excitons on the BSeD units separated from both side by fluorene segment. A significant red-shift of the emission of Se-containing copolymers in comparison with its sulfur analogue is related to the narrower $\pi-\pi^*$ gap of the BSeD unit. Stronger interchain interaction between BSeD units neighboring copolymer chains could contribute to the red shift of emission peak too. Thus, these two types of copolymers serve as good prototypes for the investigation of intra- and interchain interaction in the EL polymers. Preliminary device performance is encouraging. A device fabricated with copolymer with 15% BSeD content shows the highest EL and PL efficiency. Part of the purposes of the current work is to develop a new class of highly efficient red-emitting polymer. Preliminary results presented in this paper by using the Se-containing heterocycle in replacement of a well-investigated S analogue seems to provide a way to reach this goal. Synthesis of a series of new Se-containing EL polymers is in progress and will be reported on in subsequent publications.

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