High-Efficiency Saturated Red Emitting Polymers Derived from Fluorene and Naphthoselenadiazole

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ABSTRACT: A variety of novel light-emitting copolymers derived from 9,9-dioctylfluorene (DOF) and 2,1,3-naphthozoselenadiazole (NSeD) were prepared by the palladium-catalyzed Suzuki coupling reaction. The feed ratios of DOF to NSeD were 99.9:0.1, 99.5:0.5, 99:1, 98:2, 95:5, and 85:15. All of the polymers are soluble in common organic solvents and highly fluorescent in solid state. Devices based on the copolymers emit saturated red light, and the emission slightly red-shifted gradually with increasing NSeD's contents. The maximal external quantum efficiency of the polymer light-emitting devices (PLED) reaches 3.1%, and luminous efficiency is greater than 1.0 cd/A with emission maximum at 657 nm and Commission Internationale de L'Eclairage (CIE) coordinates of (0.64, 0.33). This is the highest efficiency with saturated red emission for a single-layer device with nonblend type emitter reported so far in the scientific literature. This indicates that the new EL polymers based on fluorene and naphthoselenadiazole are promising as a red emitter in polymer light-emitting displays.

Introduction

Since the initial discovery of conjugated polymer electroluminescence reported by Burroughes et al., polymer light-emitting diodes (PLEDs) have attracted considerable interest because of their potential application in flat panel displays.¹ PLEDs can now achieve high brightness and efficiency. Their operation lifetime is improving rapidly.² PLEDs offer advantages of low turnon and operating voltages and wide viewing angles. The range of colors available from PLEDs spans the entire visible spectrum. It is believed that PLED technology is one of the most promising for next generation largearea flat panel displays.³

Conjugated polymers with aromatic or heterocyclic units generally absorb light with wavelengths of 300-500 nm due to $\pi - \pi^*$ transitions.⁴ A high QE, a color purity, and a material stability are essential for the fullcolor flat panel application. During the past 10 years, a variety of opto-electroactive conjugated backbone structures, such as poly(*p*-phenylenevinylene) (PPV),⁵ poly-(p-phenylene) (PPP),⁶ polythiophene (PT),⁷ and polyfluorene (PF),⁸ have been prepared. Among them, poly(9,9di-n-alkylflourene) attracts special attention as a bluelight-emitting polymer, for it shows highly efficient photoluminescence (PL) and electroluminescence (EL), excellent thermal and oxidative stability, and good solubility in common organic solvents.⁸ Normally, polyfluorene homopolymers have a large band-gap and emit blue light. Significant efforts have been made to tune color to longer wavelength for fluorene-based polymers.^{9–12} Compared with a high-efficiency green polyfluorene emitter reported in the scientific literature, the polymer emitter with saturated red emission remains a great challenge. A method of tuning emission color of polyfluorenes over entire visible region is incorporating narrow band-gap comonomer into polyfluorene backbone. Most widely used narrow-band-gap comonomers are varieties of aromatic heterocycles such as thio-

phene,¹³⁻¹⁶ ethylenedioxythiophene,¹⁶⁻¹⁸ and benzothiadiazole.^{11,19–21} For example, red-emitting alternating copolymer of fluorene and 4,7-di-2-thienyl-2,1,3-benzothiadiazole (DBT) has been reported in the patent literature by the Dow Chemical group.22 Significant enhancement in efficiency (up to 1.4%) with emission peak at 663 nm for the PFO-DBT copolymer was recently reported by our group.¹¹ Cambridge Display Technology (CDT)²³ announced a saturated red emitter with high external quantum efficiency of 3% and power efficiency of 1.2 Lm/W with emission peak at 650 nm, though the detailed chemical structure was not disclosed. Recently we reported the synthesis and properties of copolymers with 9,9-dioctylflourene as a main chain building unit and the selen-containing heterocycle 2,1,3-benzoselenadiazole (BSeD) as the narrow-bandgap component.¹² We have shown that, in replacement of sulfur by selenium in the aromatic heterocycles, EL emission of the device from the resulting polymer is redshifted about 50–60 nm in comparison with the corresponding sulfur analogue. For example, devices from polyfluorene copolymer with 15% molar ratio of BSeD unit emits orange-red light with $\lambda_{max} = 582$ nm in contrast to 530 nm for copolymer with 15% of its sulfur analogue, benzothiadiazole.^{11a} To move emitter further to saturated red side, the utilization of comonomer with more narrow band gap than benzoselenodiazole is necessary.

In this paper we synthesized a new conjugated Secontaining heterocyclic monomer 2,1,3-naphthoselenadizole (NSeD) (structure in Scheme 1) which has more extended p-conjugation than benzoselenadiazole. On the basis of this new monomer, a series of novel copolymers derived from PFO and NSeD were synthesized by the palladium-catalyzed Suzuki coupling method. A special feature of Suzuki coupling is that it allows an alternating type of copolymer to be obtained in the case of A-Bcomonomers, while typical cross-coupling of dibromides provides a multiblock copolymer. In the case of Suzuki coupling, each individual narrow-band-gap unit is sepa-

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rated on both sides by wide-band-gap segments, when the narrow-band-gap component is less than or equal to 50% in the copolymer. The 2,1,3-naphthoselenadizole unit in the copolymer is isolated from both sides by fluorene host segment functions as a powerful exciton trap which allows efficient intramolecular energy transfer from the fluorene segment to the NSeD unit. Saturated red emission at the maximum wavelength of 657 nm was obtained. The highest external quantum efficiency of device fabricated with this type of copolymer is of 3.1% ph/el, and luminous efficiency is of 0.9 cd/A. To the best of our knowledge, this is the highest efficiency reported so far for nondoped fluorescent polymer LEDs in the scientific literature.

Result and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1 and Scheme 2. Monomers 2 and 3 were prepared following the already published procedure.^{22,24,25} 2,3-Diamino-1,4-dibromonaphthalene (4) was synthesized, with some modification, according to the method described by Johansson et al.²⁶ 4,7-Dibromo-2,1,3-naphthoselenadizole (5) was prepared from 4 and SeO₂ in hot ethanol.

Conjugated copolymers derived from 2,7-dibromo-9, 9-dioctylfluorene (2), 2,7-bis (4,4,5,5-tetramethyl-1,3,2dioxaborolan-2-yl)-9,9-dioctylfluorene (3), and 4,7-dibromo-2,1,3-naphthoselenadiazole (5) 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 PFO to NSeD are 99.9:0.1, 99.5:0.5, 99:1, 98:2, 95:5, and 85:15, and the corresponding copolymers are named **6a**-**f**, respectively. The resulted copolymers are readily soluble in CHCl₃, THF, and toluene. The average molec-

ular weights of these polymers are relatively high, from 8000 to 60 000 with a polydispersity index (M_w/M_n) from 2.09 to 3.09, consistent with a polycondensation reaction. The Se contents of these polymers were measured by atomic absorption spectroscopy, and the results are listed in Table 1. We note that the calculated actual copolymer composition based on independent N and Se measurements is very close to the experimental error. Once the monomer 4,7-dibromo-2,1,3-naphthoselenadiazole (5) used in the copolymerization is equal to or greater than 2%, the actual composition of the NSeD in the copolymer is remarkably reduced in comparison with that of the monomer feed ratio. The low solubility of monomer NSeD in toluene is responsible for the low NSeD incorporation ratio. The molecular weights of 6f were less than those of other copolymers. A slightly higher actual NSeD content in 0.1% feed ratio must be related to inaccuracy caused by the analytical method.

Optical Properties and Electrochemical Characteristics. The UV-vis absorption properties of the conjugated polymers based on 9,9-dioctylflourene and naphthoselenadiazole are presented in Table 2. Two absorption bands peaked at 390 and 550 nm were observed for PFO-NSeD copolymers in chloroform solution (5 \times 10⁻⁵ M) (Figure 1a). The peak positions are insensitive to NSeD content in contrast to the magnitudes of the two bands. Compared with the absorption spectrum of pure PFO, the 390 nm peak in PFO-NSeD copolymers can be identified due to fluorene segments. The intensities of the 550 nm band increase linearly with the NSeD content, suggesting that NSeD units contribute to the 550 nm absorption band. The absorption peak of 550 nm is hardly seen for copolymers with 0.1 and 0.5% NSeD content. Table 2 shows the molar absorption coefficients in CHCl₃ solution for both fluorene and NSeD peaks. The NSeD unit has a similar absorption coefficient as the fluorene unit (Table 2). This forms a sharp contrast with the polyfluorene copolymers with other narrow-band-gap comonomers, such as 2,1,3benzoselenadiazole (BSeD) and dithienbenzothiadiazole (DBT) units, which show much higher molar absorption coefficients than the fluorene segment.^{11a} As in other wide-narrow-band-gap copolymers, the narrow band unit in the solid-state films shows less absorption intensity than in the solution. Thereby the NSeD peak is much less evident for copolymers with low NSeD content (0.1-1%). Figure 1b shows that absorption spectra in solid-state film are slightly red-shifted (around 10 nm) in comparison with that in solution. From onset

Scheme 2. Synthetic Route of Copolymers



Table 1. Molecular Weights of the Copolymers and N and Se Content in the Copolymers

	Mn		N content in the feed composition	N content in the copolymers	Se content in the feed composition	Se content in the copolymers	NSeD content in the copolymers (%) according	NSeD content in the copolymers (%) according to N
copolymers	(×10 ³)	$M_{\rm w}/M_{\rm n}$	(%)	(%)	(%)	(%)	to Se content	content
PFO-NSeD 0.1 (6a)	21	2.23	0.0072	0.013	0.02	0.04	0.20	0.18
PFO-NSeD 0.5 (6b)	60	3.09	0.036	0.030	0.10	0.08	0.40	0.42
PFO-NSeD 1 (6c)	24	2.46	0.072	0.069	0.20	0.20	1.00	0.96
PFO-NSeD 2 (6d)	23	2.32	0.14	0.081	0.41	0.24	1.17	1.13
PFO-NSeD 5 (6e)	18	2.09	0.37	0.28	1.02	0.40	1.96	3.82
PFO-NSeD 15 (6f)	8	2.61	1.15	0.82	3.25	2.02	10.86	9.54

Table 2. UV-Vis Properties of Copolymers in CHCl₃

		molar absorption coeff, $\epsilon^a ({ m mol}^{-1} { m L} { m cm}^{-1})$		
copolymers	$\lambda_{\rm abs}/{\rm nm}$	fluorene	NSeD	
PFO-NSeD 0.1 (6a)	391 301	$2.67 imes 10^4$ $2.71 imes 10^4$		
PFO-NSeD 1 (6c)	385, 556	3.85×10^4	1.8×10^4	
PFO-NSeD 2 (6d) PFO-NSeD 5 (6e) PFO-NSeD 15 (6f)	390, 559 389, 555 353, 563	$3.47 imes 10^4 \ 2.69 imes 10^4 \ 3.30 imes 10^4$	$3.80 imes 10^4 \ 3.47 imes 10^4 \ 5.53 imes 10^4$	

^{*a*} Molar absorption coefficient of each comonomer was calculated according to the equation $\log(I_0/I) = \epsilon cd$, where ϵ is the molar absorption coefficient and *c* is the molar concentration of corresponding chromophore (moles of fluorene or NSeD unit in a liter of copolymer solution (mol/L)).



Figure 1. (a) UV–vis absorption spectra for the copolymers in the CHCl₃ solution (5 \times 10⁻⁵ M). (b) UV–vis absorption spectra for the copolymers in solid-state films.

of two peaks we can estimate the optical band gap corresponding to fluorene segment and NSeD unit at around 3.0 and 2.0 eV, respectively (Table 3).

The electrochemical behavior of the copolymers was investigated by cyclic voltammetry (CV) (Figure 2). Table 3 summarizes oxidation and reduction potentials derived from the onset in the cyclic voltammograms of the copolymers. We can record only one p-doping process and one n-doping process. The onset of oxidation process is about 1.32-1.40 V, which is very close to the data reported for polyfluorene homopolymer, $E_{ox} = 1.4$ V and $I_{\rm p} = 5.8 \, {\rm eV}.^{27}$ This peak is attributed to p-doping of PFO segments. The onset of n-doping processes of copolymers is -(0.72-0.78) V. Since the reduction potential for polyfluorene homopolymer was observed typically at 2.28 V,²⁷ the reduction wave at -(0.72-0.78) V must be attributed to the reduction process for the NSeD unit. We were unable to record a second reduction wave corresponding to the fluorene segment. It is probably due to the instability of the reduced state of these copolymers at higher negative voltage. HOMO and LUMO levels calculated by empirical formulas (E_{HOMO} $= -e(E_{\text{ox}} + 4.4) \text{ eV} \text{ and } \vec{E}_{\text{LUMO}} = -e(E_{\text{red}} + 4.4) \text{ eV}^{28}$ are also listed in Table 3. The HOMO and LUMO levels are almost identical for copolymer of different composition. From the obtained oxidation and reduction potential, we estimate electrochemical band gap at ca. 2.06-2.16 eV for copolymers (Table 3). This value is close to the optical band gap determined for NSeD unit from absorption spectra in the solid film (Table 3).

Photoluminescence Properties. Photoluminescence spectra (Figure 3a) of copolymers in 1×10^{-3} M solution of chloroform were taken under an excitation of 325 nm by using a Fluorolog-3 spectrofluorometer (Jobin Yvon). At this concentration, PL response is dominated by PFO segment for copolymers PFO-NSeD0.1 and PFO-NSeD0.5. For copolymer PFO-NSeD1 an additional PL emission peak can be observed at around 700 nm. The intensity of this PL peak increases with increasing the NSeD concentration in the copolymers. We can attribute the 700 nm emission to the NSeD unit. This indicates that the efficient energy transfer from the excitons created on the PFO segment to the narrow-band-gap unit, NSeD, is highly efficient. Figure 3b shows the dependence of PL profile of copolymer PFO-NSeD5 on the copolymer concentration in the CHCl₃ solution. The PL peak at 700 nm increases dramatically with increasing copolymer concentration in the solution. We note that even at a very high concentration of 1×10^{-3} m/L the considerable contribution of PFO emission remains. Compared with PFO-DBT copolymer reported previously,^{11a} complete quenching of host emission was observed at a dilute concentration of 4×10^{-4} m/L for the copolymer of PFO–DBT1 in the solution. This indicates either less efficient intrachain energy transfer in PFO-NSeD copolymer or less interchain interaction between PFO-NSeD chains in the solution. The photoluminescence (PL) spectra of the copolymers in thin film, produced under the excita-

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copolymers	optical band gap ^b /eV	band gap ^c /eV	$E_{\rm ox}/{ m V}$	$E_{\rm red}/{\rm V}$	HOMO/eV	LUMO/eV
PFO ^a	2.95	3.61	1.39	-2.22	-5.79	-2.18
PFO-NSeD 0.1 (6a)	2.95	2.16	1.38	-0.78	-5.78	-3.62
PFO-NSeD 0.5 (6b)	2.95	2.14	1.36	-0.78	-5.76	-3.62
PFO-NSeD 1 (6c)	2.95	2.12	1.40	-0.72	-5.80	-3.68
PFO-NSeD 2 (6d)	2.95	2.12	1.36	-0.76	-5.76	-3.64
PFO-NSeD 5 (6e)	2.95, 1.96	2.08	1.34	-0.74	-5.74	-3.66
PFO-NSeD 15 (6f)	2.95, 1.95	2.06	1.32	-0.74	-5.72	-3.66

Table 3. UV-Vis Properties and Electrochemical Properties of the Copolymers

^{*a*} Polyfluorene (PFO) homopolymer. ^{*b*} Estimated from the onset wavelength of optical absorption in solid-state film. ^{*c*} Calculated from oxidation and reduction potential.



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

tion of 325 nm line of the HeCd laser, are presented in Figure 3c. Similar to the PL emission in solution, PL spectra in the solid state consist of two peaks corresponding to both fluorene and NSeD segments, respectively. For PFO-NSeD0.1, the PL spectrum was dominated by PFO emission, while the emission of NSeD at 634 nm was very weak. The intensity of the 660-700 nm peak increases dramatically with increasing NSeD composition in the copolymer in the solid state. For the copolymer PFO-NSeD0.5 the relative intensities of PFO and NSeD components become equal (Figure 3c). When NSeD content in the copolymer increases to 1% (PFO–NSeD1), PFO emission decreases significantly. Since PFO-NSeD1 has an average molecular weight $M_{\rm n} = 24\,000$, around 62 units per chain (Table 1), statistically, only two copolymer chains from three can have one NSeD unit in a chain, while one out of three polymer chains should be PFO homopolymer. To completely quench PFO emission including PFO homopolymer, interchain interaction (interchain energy transfer) is absolutely necessary in this case. By comparing PL spectra in the solution and in the solid state (Figure 3a,c), it is obvious that the relative intensity of NSeD to PFO in the solid state (Figure 3c) is much higher than that in solution. This clearly indicates the importance of interchain interaction in this case. PFO emission in the solid-state film was completely guenched for PFO-NSeD5. We note that for the PFO–DBT copolymer^{11a} PFO emission at solid state was completely quenched at concentration of 1% of DBT content in the copolymer PFO-DBT1. This fact again indicates that the interchain interaction between PFO-NSeD chains is weaker

than that of its sulfur analogue, probably due to a great Se radius.

In Table 4, we list the absolute PL efficiency measured in the integrating sphere and the maximum emission wavelength of the copolymer in a thin film. The PL efficiency initially increases with increasing the NSeD content, reaching a maximum of 84% for PFO-NSeD2. With further increase in NSeD content to 5% the PL efficiency starts to decrease. The initial increase in PL efficiency is probably due to disturbing PFO chain regularity by incorporation of big size Se-containing heterocycles. The further decrease in PL efficiency after passing maximum is due to concentration quenching of heavy metals. We note in the report by Hou et al.^{11a} that PL efficiency of PFO–DBT copolymer has a much lower PL efficiency (11.4 and 12.5% for PFO-DBT1 and PFO-DBT5, respectively) than the Se-containing polymer. This again indicates that the interchain interaction for Se-containing copolymers is remarkably reduced due to large Se atomic size in comparison with its sulfur analogue.

Electroluminescence Properties. Devices from PFO-NSeD copolymers are fabricated with configuration ITO/PEDT/PFO-NSeD/Ba/Al. Figure 5 shows EL spectra of such devices. In contrast to PL spectra, EL emission consists exclusively of red emission peaked at around 640–670 nm originating from the NSeD unit for copolymers with NSeD content equal to or greater than 0.5%. PFO host emission is completely quenched at 0.5% NSeD concentration in the copolymer. Even for copolymer PFO-NSeD0.1, EL emission responsible for PFO emission in the region of 400-460 nm is much weaker than the emission at 640 nm originating from the NSeD unit. The emission peaks are red-shiftted from 634 nm for PFO-NSeD0.1 to 672 nm for PFO-NSeD15. McGehe²⁹ and O'Brien³⁰ reported a large difference between PL and EL spectra at low doping concentration region for Eu-complex/CNPPP and PtOEP/PFO devices, respectively. For these systems the host PL emissions were quenched completely only at much higher doping concentration than that for EL spectra. They explained that the difference between PL and EL processes has a different recombination zone. Recently, many authors^{31–33} attributed similar results observed for phosphorescent dye-doped PLEDs to that the dominant emission mechanism in phosphorescent dye-doped PLEDs is charge trapping (rather than Förster transfer) followed by recombination on Ir-complex molecules. According to Gong et al.,³³ the hole and electron trapping mechanism is most favorable if the HOMO level of the guest is above that of the host and if LUMO level of the guest is below that of the host. This argument can be used for intramolecular trapping systems. The LUMO level of the NSeD unit in PFO-NSeD copolymer is around 3.70 eV, much less than the LUMO level of PFO homopolymer (2.7 eV). The HOMO level of PFO-NSeD copolymer is



Figure 3. (a) PL spectra of PFO–NSeD copolymers in solution $(1 \times 10^{-3} \text{ M} \text{ in chloroform})$. (b) PL spectra of PFO–NSeD5 copolymers in chloroform solution with different concentrations of copolymer. (c) PL spectra for the copolymers in the thin films.

around 5.7 eV (Table 1), which is slightly above the HOMO of the host 5.77 eV. Thus, energy level alignment of guest and host components in the copolymer chain is favorable for intra- and intermolecular trapping in the PFO–NSeD copolymers.

On the basis of the results described above, the concentration dependence of PL spectra in solution and solid state (Figure 3), and EL spectra of copolymer of different composition (Figure 4), we conclude that energy transfer from host PFO segment to NSeD unit

 Table 4. Absolute PL Efficiencies Measured in the Integrating Sphere

polymers	λ_{Plsmax}/nm	Q _{PLsmax} (%)
PFO	432	47.0
PFO-NSeD 0.1 (6a)	423, 634	33.0
PFO-NSeD 0.5 (6b)	438, 645	68.7
PFO-NSeD 1 (6c)	423, 647	77.4
PFO-NSeD 2 (6d)	420, 656	84.0
PFO-NSeD 5 (6d)	421, 671	52.7
PFO-NSeD 15 (6f)	422, 681	33.6

in PFO–NSeD copolymer occurs mainly via intramolecular trapping, which must be a very quick and efficient process. Intermolecular interaction is also important for low-NSeD content copolymers (<0.5%).

The external EL efficiencies in the device of configuration ITO/PEDT/PFO-NSeD/Ba/Al vary with the copolymer composition. The device performance is listed in Table 5. The external quantum efficiencies (EQE) increase initially with NSeD content and then decrease. The best device performance is observed for devices fabricated with PFO-NSeD1 copolymer. It is worthwhile to note that dependence of EL efficiency on the copolymer composition coincides with the PL change pattern (Table 3). Figure 5 shows external quantum efficiency and luminance as a function of current density for device with PFO-NSeD1. As can be seen from Figure 5, the device shows a high external quantum efficiency of around 3.0% without significant decay in efficiency over wide range up to high current density (270 mA/cm²). The highest external EL quantum efficiencies was 3.1% and luminous efficiency of 0.91 cd/A with the luminance of 906 cd m⁻² at current density of 98 mA/cm² and at the bias voltage of 8.9 V (Table 4). The highest luminance can reach 2104 cd m⁻² at 9.8 V. To the best of our knowledge, this is the highest efficiency with saturated red emission for a single-layer device with nonblend type emitter reported so far in the scientific literature.

Conclusion

A novel EL polymer, poly(9,9-dioctylfluorene-co-naphthoselenadiazole), was successfully synthesized. The efficient energy transfer due to exciton trapping on narrow-band-gap NSeD sites has been observed. EL emission from PFO segment was completely quenched at very low NSeD content (0.5%). Saturated red emission at the maximum wavelength of 657 nm was obtained. The highest external quantum efficiency is of 3.1% photon/electron, and luminous efficiency is of 0.9 cd/A with 908 cd/m². To the best of our knowledge, this is the highest efficiency reported so far for nondoped fluorescent polymer LEDs. We further demonstrated that improvement in PL and EL efficiency in comparison with its sulfur analogue could be attributed to the reduction in interchain interaction due to larger atomic size of the selenium atom.

Experimental Section

Materials and Measurement. 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 were used as received. All solvents were carefully dried and purified under nitrogen flow. ¹H and ¹³C NMR spectra were recorded on a Varian Inova 500 or Bruker DRX 400 spectrometer operating respectively at 500 and 100 MHz and were referenced to tetramethylsilane. GPC was obtained through a Waters GPC 2410 in tetrahydrofuran using a calibration curve



Figure 4. EL spectra of PFO-NSeD copolymers.



Figure 5. External quantum efficiency and luminance of ITO/ PEDT/PFO-NSeD1/Ba/Al device.

of polystyrene standards. Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.) or an ANTEK7000 elemental analysis instrument (ANTEK Co.). The elemental selenium analysis was recorded on a polarized Zeeman atomic absorption spectrophotometer (Hitachi Co., Japan). UV-vis absorption spectra were recorded on a HP 8453 spectrophotometer. The PL quantum yields were determined in an Integrating Sphere IS080 (LabSphere) with 325 nm excitation of a HeCd laser (Melles Griot). PL an EL spectra were recorded on an 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 a calomel reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile $(CH_3CN).$

2,7-Dibromofluorene (1).²² Bromine (31.4 g, 0.196 mol) in 20 mL of chloroform was added dropwise into a suspension solution containing fluorene (15.0 g, 0.091 mol), iron power (80 mg, 1.43 mmol), and 100 mL of chloroform. The flask was cooled by ice water, and the temperature was controlled under 5 °C. The reaction was allowed to stand for 2 h. The product was filtered and recrystallizd with chloroform, giving white crystal (27.3 g, 93.2%); mp 161–163 °C.

2,7-Dibromo-9,9-dioctylfluorene (2).²² 1-Bromooctane (18.6 g, 0.097 mol) was dropped into a suspension of **1** (15.0 g, 0.046 mol) and benzyltriethylemmonium chloride (0.09 g 0.39 mmol) in DMSO (200 mL) and sodium hydroxide (15 mL of 50 wt %). The mixture was stirred vigorously for 3 h at a room

temperature and extracted with ether. The extract was washed with saturated sodium chloride solution and dried with anhydrous magnesium sulfate. Evaporation of the solvent and purification by flash column with hexane as eluent gave with crystal; mp 49–50 °C.

2,7-Bis(4,4,5,5-tetramathyl-1,3,2-dioxaborolan-2-yl)-9,9dioctylfluorene (3). n-Butyllithium (23 mL of a 1.6 M solution in hexane, 36.8 mmol) was added dropwise into a solution of 2 (6.0 g, 10.9 mmol) in tetrahydrofuran (THF,150 mL) at -78 °C under an atmosphere of dry argon. The mixture was stirred at -78 °C for 1 h, and then 2-isopropoxy-4,4,5,5tetramethyl-1,3,2-dioxaborolane (25 mL, 123.24 mmol) was injected promptly into the flask. The mixture was stirred at -78 °C for 2 h, and then the reaction was allowed to stand overnight at room temperature. The mixture was poured into water and was extracted with ether. The extract was washed with brine and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was recrystallized from THF and methanol and gave a white crystal (5.2 g, 74.0%); mp 128–130 °C. ¹H NMR (500 MHz, CDCl₃): δ (ppm): 7.83 (d, 2H), 7.75 (d, 2H), 1.92 (m, 4H), 1.35 (s, 24H), 1.25-1.01 (m, 20H), 0.81 (t, 6H), 0.60 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.92, 144.50, 134.90, 128.92, 119.54, 82.53, 55.54, 41.05, 32.78, 30.40, 29.61, 25.41, 44.10, 23.20, 14.78. Anal. Calcd for C41H64O4B2: C, 76.74; H, 10.04. Found: C, 76.68; H, 10.15.

1,4-Dibromo-2,3-diaminoaphthalene (4). A mixture of 0.75 mL of bromine (2.36 g, 14.7 mmol) and 20 mL of glacial acetic acid was added dropwise into a solution of 1.04 g of 2,3-diaminophthalene (6.58 mmol) in 30 mL of glacial acetic, with vigorous stirring at room temperature. After 1 h, the precipitate was filtered and washed subsequently with 50 mL of glacial acetic acid, 100 mL of 2 wt % sodium carbonate solution, and 100 mL of water. A yellow powder was obtained after drying (1.84 g, 88.5%); mp 95–97 °C. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 8.02 (q,2H), 7.41 (q, 2H), 4.33 (s, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 134.94, 128.27, 126.08, 125.43, 106.90. Anal. Calcd for C₁₀H₈Br₂ N ₂: C, 37.97; H, 2.53; N, 8.86. Found: C, 38.50; H, 2.60; N, 9.01.

4,7-Dibromo-2,1,3-naphthoselenadizole (5). A solution of selenious oxide (0.34 g, 3.06 mmol) in 10 mL of water was added dropwise into a mixture of **4** (0.8 g, 2.53 mmol) and 200 mL of ethanol at 70 °C, and the temperature was maintained for 2 h. The mixture was cooled to room temperature overnight, and the precipitate was filtered and recrystallized in acetic ether and gave a purple solid (0.91 g, 91%); mp 264–265 °C.

		device performance				
copolymers	CIE x, y	$\lambda_{\rm max}$ (EL)/nm	bias/V	current density/mA cm ⁻²	luminance/cd m^{-2}	QE _{ext} (%)
PFO-NSeD 0.1 (6a)	0.37, 0.34	634	6.7	30.0	1870	0.56
PFO-NSeD 0.5 (6b)	0.61, 0.35	645	6.27	33.3	980	0.30
PFO-NSeD 1 (6c)	0.64, 0.33	657	8.9	98.0	908	3.10
PFO-NSeD 2 (6d)	0.67, 0.32	659	7.6	7.3	22.5	1.14
PFO-NSeD 5 (6e)	0.68, 0.31	662	13.1	33.3	165	0.35
PFO-NSeD 15 (6f)	0.69, 0.30	672	6.7	33.3	20.3	0.22

¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.48 (d,2H), 8.29 (d,2H). Anal. Calcd for C₁₀H₄Br₂N₂Se: C, 30.69; H, 1.02; N, 7.16; Se, 20.20. Found: C, 30.84; H, 1.16; N, 7.31; Se, 20.05.

General Procedure of Polymerization. Carefully purified 2,7-dibromo-9,9-dioctylfluorene (2), 2,7-bis(4,4,5,5-tetramathyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (3), 4,7dibromonaphthoselenadizole (5), (PPh₃)₄Pd(0) (0.5-2.0 mol %), and several drops of Aliquat 336 were dissolved in a mixture of toluene and aqueous 2 M Na₂CO₃. The solution was refluxed with vigorous stirring for 72 h under an argon atmosphere. At the end of polymerization, 2,7-bis(4,4,5,5-tetramathyl-1,3,2dioxaborolan-2-yl)-9,9-dioctylfluorene was added to remove bromine end groups, and bromobenzene was added as a monofunctional end-capping reagent to remove boracic ester end group because boron and bromine units could quench emission and contribute to excimer formation in LED application. The mixture was then poured into methanol. The precipitated material was filtered and washed for 24 h with acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF, CHCl₃, and toluene. Yield: 45 - 80%.

Poly[2,7-(9,9-dioctylfluorene)-*co***-4,7-(2,1,3-naphthose-lenadizole)**] **(6a)**. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-2-yl)-9,9-dioctylfluorene **(3)** (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene **(2)** (0.499 equiv), and 4,7-dibromo-2,1,3-benzoselenadiazole **(5)** (0.001 equiv) were used in this polymerization. Element Anal. Found: C, 89.55%; H, 10.92%; N, 0.013%. Atomic absorption spectra for Se: 0.04%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.86, 7.70, 2.15, 1.55,1.16–1.22, 0.83. ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.21, 140.90, 140.43, 126.55, 121.89, 120.36, 55.74, 40.79, 32.19, 30.43, 29.62, 24.31, 23.00, 14.46.

Poly[2,7-(9,9-dioctylfluorene)-*co***-4**,**7-(2,1,3-naphthose-lenadizole)] (6b).** 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**2**) (0.495 equiv), and 4,7-dibromo-2,1,3-benzoselenadiazole (**5**) (0.005 equiv) were used in this polymerization. Element Anal. Found: C, 88.41%; H, 10.48%; N, 0.03%. Atomic absorption spectra for Se: 0.08%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.84, 7.70, 2.15, 1.55, 1.16–1.27, 0.83. ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.21, 140.91, 140.41, 126.58, 121.88, 120.32, 55.74, 40.80, 32.19, 30.40, 29.62, 24.33, 23.00, 14.47.

Poly[2,7-(9,9-dioctylfluorene)-*co***-4,7-(2,1,3-naphthose-lenadizole)] (6c).** 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**2**) (0.49 equiv), and 4,7-dibromo-2,1,3-benzo-selenadiazole (**5**) (0.01 equiv) were used in this polymerization. Element Anal. Found: C, 88.21%; H, 10.15%; N, 0.069%. Atomic absorption spectra for Se: 0.20%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.82, 7.66, 7.55, 7.45, 7.33, 7.01, 2.11, 1.12–1.23, 0.79, 0.52. ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.21, 140.92, 140.06, 126.54, 121.80, 120.35, 55.74, 32.19, 30.44, 29.63, 24.35, 23.00, 16.05, 14.47.

Poly[2,7-(9,9-dioctylfluorene)-*co***-4**,**7-(2,1,3-naphthose-lenadizole)] (6d).** 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-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-benzo-selenadiazole (**5**) (0.02 equiv) were used in this polymerization. Element Anal. Found: C, 87.60%; H, 10.23%; N, 0.081%. Atomic absorption spectra for Se: 0.24%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.86, 7.70, 2.14, 1.56, 1.16, 0.84, 0.63. ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.83, 140.53, 140.03,

126.17, 121.53, 119.95, 55.35, 40.39, 31.79, 30.04, 29.21, 24.35, 23.94, 22.95, 14.03.

Poly[2,7-(9,9-dioctylfluorene)-*co***-4**,**7-(2,1,3-naphthoselenadizole)] (6e).** 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-2-yl)-9,9-dioctylfluorene (**3**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**2**) (0.45 equiv), and 4,7-dibromo-2,1,3-benzo-selenadiazole (**5**) (0.05 equiv) were used in this polymerization. Element Anal. Found: C, 87.05%; H, 9.98%; N, 0.28%. Atomic absorption spectra for Se: 0.40%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.82, 7.66, 7.50, 7.01, 2.11, 1.37, 1.12–1.23, 0.80. ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.21, 140.90, 140.26, 126.48, 121.85, 120.36, 55.74, 32.19, 30.44, 29.63, 24.35, 23.00, 14.47.

Poly[2,7-(9,9-dioctylfluorene)-*co***-4,7-(2,1,3-naphthose-lenadizole)] (6f).** 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lan-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-benzo-selenadiazole (**5**) (0.15 equiv) were used in this polymerization. Element Anal. Found: C, 86.02%; H, 8.86%; N, 0.82%. Atomic absorption spectra for Se: 2.02%. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 7.85, 7.70, 7.51, 2.15, 1.59, 1.43, 1.36, 1.16, 1.50, 0.84, 0.73. ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 151.82, 140.54, 140.03, 126.17, 121.52, 119.96, 55.35, 40.36, 31.78, 30.03, 29.201, 24.95, 22.58, 14.02.

Device Fabrication and Characterization. LED was fabricated on prepatterned indium-tin oxide (ITO) with sheet resistance $10-20 \ \Omega/\Box$. The substrate was ultrasonically cleaned with acetone, detergent, deionized water, and 2-propanol, subsequently. Oxygen plasma treatment was taken for 10 min as the final step of cleaning to improve the contact angle just before film forming. Onto the ITO glass a layer of poly(ethylenedioxythiophene)-poly(styrenesulfonic acid) (PEDOT:PSS) film with a thickness of 50 nm was spin-coated from its aqueous dispersion (Baytron P 4083, Bayer AG), aiming to improve the hole injection and to avoid possibility of leaking. Solution of PFO-NSeD copolymers in toluene were prepared in nitrogen-filled drybox and spin-coated on top of the ITO/PEDOT:PSS surface. A typical thickness of emitting layer was 70-80 nm. Then a thin layer of barium as an electron injection cathode, and subsequently 200 nm aluminum protection layers were thermally deposited by vacuum evaporation through a mask at a base pressure below 2×10^{-4} Pa. The deposition speed and the thickness of the barium and aluminum layers were monitored with a thickness/rate meter model STM-100 (Sycon Instrument, Inc.). The cathode area defines the active area of the device. A typical active area of devices in this study is 0.15 mm². The EL layer spin-coating process and the device performance tests were taken within a glovebox (Vacuum Atmosphere Co.) with nitrogen circulation. $\tilde{I}-V$ characteristics were measured with a computerized Keithley 236 source measure unit. The luminance of device was measured with calibrated photodiode. The external quantum efficiency was verified by measurement in the integrating sphere (IS-080, Labsphere), and luminance was calibrated by using a PR-705 SpectraScan spectrophotometer (Photo Research) after encapsulation of devices with UV-curing epoxy and thin cover glass.

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