

Synthesis and Properties of Novel Deep Red-emitting Copolymers Based on a Poly(*p*-phenylenevinylene) Derivative

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ABSTRACT: A series of novel copolymers based on a poly(*p*-phenylenevinylene) (PPV) derivative with different content of narrow band-gap unit 2,1,3-benzoselenadiazole-vinylene (BSeV) was prepared via Stille coupling reaction. The copolymers emit light from deep red to near-infrared (NIR) depending on BSeV content in the copolymers. The electroluminescence (EL) emission peaked at 752 nm for the copolymer with the content of 30 mol % BSeV is among the longest reported so far for the PPV polymers.

The best device performance is observed for the copolymer with 1 mol % BSeV content with external quantum efficiency (QE_{ext}) of 0.26% and CIE coordinate 0.65, 0.34 (x, y). © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4321–4327, 2006

Key words: poly(*p*-phenylenevinylene) (PPV); narrow band-gap; Stille coupling reaction; electroluminescence; polymer light-emitting diodes (PLEDs)

INTRODUCTION

It is extremely important to have saturated emission to realize full-color flat panel displays and deep-red and near-infrared (NIR)-responded conjugated polymers for photovoltaic devices to match solar-terrestrial radiation.^{1–3} Because of their excellent properties and potential applications, poly(*p*-phenylenevinylene) (PPV) and its derivatives have attracted much attention in the past few years.^{4,5} However, although ceaseless efforts and great success have been made to tune the emission color, the peak emission wavelength reported by early works on PPV derivatives was below 620 nm.^{4–9} There were several papers reporting devices from PPV derivatives with the maximal electroluminescence (EL) emission extending over 700 nm by attaching strong electron-withdrawing group to the PPV main chain, such as CN-PPV derivatives.^{10,11} However, the stability of such polymers is still an unsettled question. To obtain novel saturated red light-emitting PPV-based polymers without electron-withdrawing substituents, we have recently prepared a series of novel PPV-based copolymers by incorporating a well-

controlled S-containing heterocyclic comonomer 2,1,3-benzothiadiazole (BT)¹² 4,7-bis(2-thienyl)-2,1,3-benzothiadiazole (DBT)¹³ into the polymer main chain of poly(2-methoxy-5-octyloxy-*p*-phenylenevinylene) (PMOPV). The emissions of Se-containing copolymers were more red-shifted than those of S-containing copolymers, and most emissions were in NIR region.¹³ Yang et al. also reported that replacing S in benzothiadiazole by Se led to significant red shift of the resulting polyfluorene-benzoselenadiazole copolymers.³ In this paper, 2,1,3-benzoselenadiazole (BSe) has been introduced into PMOPV main chain by Stille cross-coupling condensation. A novel PPV-based copolymer containing the host segment of 2-methoxy-5-octyloxy-*p*-phenylenevinylene (MOPV) and the unit of BSeV give off red- and NIR-light emission depending on comonomer composition. Chemical and photophysical characterization of the resulting copolymers were presented. Preliminary device performances of these copolymers were also reported.

EXPERIMENTAL

Materials and characterization

All reagents, unless otherwise specified, were purchased from Aldrich, Acros and TCI and were used without further purification. All solvents were carefully dried and purified in nitrogen flow. All manipulations involving air-sensitive reagents were performed in an atmosphere of dry argon. 1-Methoxy-4-octyloxypheny-

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lene (1), 2,5-dibromo-1-methoxy-4-octyloxyphenylene (2), and PMOPV used in this study were synthesized by the same procedure as was described in our previous work.^{12,13}

¹H and ¹³C-NMR spectra were recorded on a Bruker DRX 400 spectrometer operating respectively, at 400 and 100 MHz, and were referenced to tetramethylsilane. GPC was obtained through a Waters GPC 2410 in tetrahydrofuran using a calibration curve of polystyrene standards. Elemental analyses were performed on Vario Elemental Analysis Instrument (Elementar Co.) or ANTEK7000 Elemental Analysis Instrument (Antek Co.). Cyclic voltammetry was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV/s against saturated calomel reference electrode with nitrogen-saturated solution of 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in acetonitrile (CH₃CN). The UV-Vis absorption spectra were recorded by a HP8453A spectrophotometer.

Device fabrication and test were made in a glove box (VAC) with circulating nitrogen. The device structure for the copolymers is ITO/PEDOT : PSS/copolymer/Ba/Al fabricated on indium tin oxide (ITO) coated glass substrates. The layer of polyethylene dioxythiophene doped with polystyrene sulfonate (PEDOT : PSS, Baytron P 4083, Bayer AG) film with a thickness of 60 nm was spin-coated on the top of ITO as a hole injection layer.¹⁴ The copolymer layer has a thickness of 80 nm. A 4-nm thick layer of barium as a cathode and a 200-nm thick aluminum protection layer were then thermally evaporated on the top of the copolymer. The current-voltage (I-V) and luminance-voltage (L-V) characteristics were collected by a computerized Keithley 236 source meter and a calibrated silicon photodiode. Luminance was calibrated by photometer PR705 (Photo Research). External EL quantum efficiency was taken in the integrating sphere (Model IS080, Labsphere). The EL and PL spectra were recorded by Oriel INTASPEC IV CCD spectroscopy with fiber probe. External EL quantum efficiency and absolute PL efficiency using a 488-nm line of Argon ion laser were measured in an integrating sphere.

Synthesis of 4,7-dibromo-2,1,3-benzoselenadiazole (3)¹⁵

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 stirred at room temperature for 75 min, the precipitate of silver bromide was filtered off, and the filtrate was 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. MS: m/z 341.

¹H-NMR (400 MHz, CDCl₃), δ (ppm): 7.63 (s, 2H, phenylene ring). ¹³C-NMR (100 MHz, CDCl₃), δ (ppm): 157.2, 132.1, 116.5.

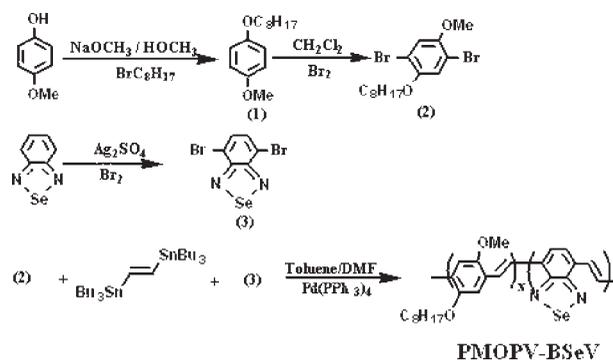
General procedure of polymerization

Trans-1,2-bis(tri-*n*-butylstannyl)ethylene (TCI), Pd(PPh₃)₄ (0.5–1.5 mol %) and carefully purified 2,5-dibromo-1-methoxy-4-octyloxyphenylene (2) and 4,7-dibromo-2,1,3-benzo-selenadiazole (3) were dissolved in a mixture of toluene and DMF (2 : 1 v/v). The solution was refluxed by 48-h vigorous stir in an argon atmosphere.^{16–18} At the end of polymerization, benzene boric acid and bromobenzene were, respectively, added to remove the end groups of tri-*n*-butylstannyl¹⁷ and bromine,¹⁹ thus avoiding quenching emission and generating excimers in PLEDs.¹⁹ The mixture was then poured into ethanol. The precipitate was filtered off, washed with acetone, and purified by column chromatography (silica gel, toluene). The resulting polymers PMOPV-BSeV were readily soluble in common organic solvents, such as THF, CHCl₃, and toluene. Yield: 80–95% respectively.

RESULTS AND DISCUSSION

Synthesis and chemical characterization

The dibromide comonomers were prepared according to general procedures.^{12,13,15} Conjugated copolymers PMOPV-BSeV are prepared via palladium-catalyzed Stille coupling reaction (Scheme 1).^{16–18} On the basis of GPC, the number-average molecular weights (M_n) of these polymers are estimated at 4300–5000 with a polydispersity index (M_w/M_n) from 2.47 to 2.95 (Table I). The starting comonomer ratios have been adjusted to investigate the effect of copolymer composition on the physical and optical properties. In the polymerization reaction, molar amount of *trans*-1,2-bis(tributylstannyl)ethylene is always equal to the sum of two comonomers of 2-methoxy-5-octyloxyphenylene (MOP) dibromide and BSe dibromide, thus obtaining PPV main chain structure. The actual



Scheme 1 Synthetic route of monomers and polymers.

TABLE I
Molecular Weights of the Copolymers and Copolymer Composition

Copolymers	M_n ($\times 10^3$)	M_w/M_n	C ^a (%)	H ^a (%)	N ^a (%)	MOP : BSe in the feed ratios	MOP : BSe in the copolymers ^b
PMOPV	4.9	2.52	78.69	9.28	–	–	–
PMOPV-BSeV0.5	5.0	2.60	78.02	9.16	0.04	99.5 : 0.5	99.6 : 0.4
PMOPV-BSeV1	5.0	2.47	77.86	9.14	0.09	99 : 1	99.2 : 0.8
PMOPV-BSeV5	4.9	2.51	76.92	8.92	0.50	95 : 5	95.4 : 4.6
PMOPV-BSeV15	4.5	2.84	74.90	8.45	1.40	85 : 15	87.3 : 12.7
PMOPV-BSeV30	4.3	2.95	69.57	7.47	2.74	70 : 30	75.1 : 24.9

^a Results of elemental analysis.

^b Calculated from results of elemental analysis.

ratios of MOP to BSe of the copolymers calculated from the elemental analysis are listed in Table I, which are very close to the feed ratios except the copolymers with large BSe feed ratios, which may be due to the low solubility of BSe dibromide in the reaction solution. The feed ratios of the comonomers and the results of elemental analysis of copolymers are listed in Table I. The copolymers have been characterized by ¹H-NMR and ¹³C-NMR with CDCl₃ as the solvent. Chemical shifts are roughly similar for all copolymers except that the ¹H chemical shifts at ca. δ 7.65 ppm appear for the copolymers with high BSeV content which represent the H atoms on the benzoselenadiazole ring, while they are not clearly observed for the copolymers with low BSeV content. The adscription of chemical shifts for the copolymers are similar to our previous work.¹² The representative ¹H-NMR spectra of PMOPV-BSeV0.5 and PMOPV-BSeV5 are shown in Figure 1.

Optical and electrochemical properties

The optical and electrochemical properties of PMOPV-BSeV are very similar to those of poly(2-methoxy-5-octyloxy-*p*-phenylenevinylene-*co*-2,1,3-benzothiadiazolevinylene) (PMOPV-BTV).¹² Maximal wavelengths of the absorption peaks, optical band gaps and electrochemical properties of the conjugated PMOPV-BSeV copolymers are given in Table II. Figure 2 compares the normalized UV-Vis absorption of the polymers in the thin solid films [Fig. 2(a)] and in chloroform solution (5×10^{-5} mol/L, average molar (repeated unit) concentration) [Fig. 2(b)]. Two distinct absorption bands are observed in the copolymers with high content of BSeV units. The absorption peak of 485 nm and the shoulder peak of about 580 are, respectively, assigned to the absorption of the MOPV segment and the BSeV unit. Absorption spectra in the solution [Fig. 2(b)] are quite similar to the solid spectra [Fig. 2(a)] except that the absorption edge in the solution is significantly blue-shifted in around 50 nm. The optical band gaps deduced from the onset of the absorption of PMOPV-

BSeV in the solid film are about 1.72–1.70 eV, which is almost unchanged with increasing the BSeV content for copolymers with BSeV content equal to or greater than 5% [Fig. 2(a) and Table II].

The electrochemical behavior of the copolymers was investigated by cyclic voltammetry (CV). The onset of *p*-doping and *n*-doping processes for PMOPV is, respectively, about 0.55 and –1.58 V. Only one *p*-doping process and one *n*-doping process of all copolymers are recorded. The oxidation wave can be attributed to *p*-doping of the MOPV segment in the copolymers. The onset of the reduction wave decreases gradually with increasing the BSeV content in the copolymers (Table II) and can be attributed to the reduction of BSeV unit. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels are calculated by the empirical formulas $E_{\text{HOMO}} = -\exp(E_{\text{ox}} + 4.4)$ (eV) and $E_{\text{LUMO}} = -\exp(E_{\text{red}} + 4.4)$ (eV).²⁰ The calculated results indicate that the HOMO levels of the copolymers depend on the MOPV segment, while the LUMO levels are coupled with BSeV units.^{12,13} Electrochemical band-gap estimated from HOMO and LUMO levels as around 2 eV are slightly greater than that of optical band-gap (1.7 eV).

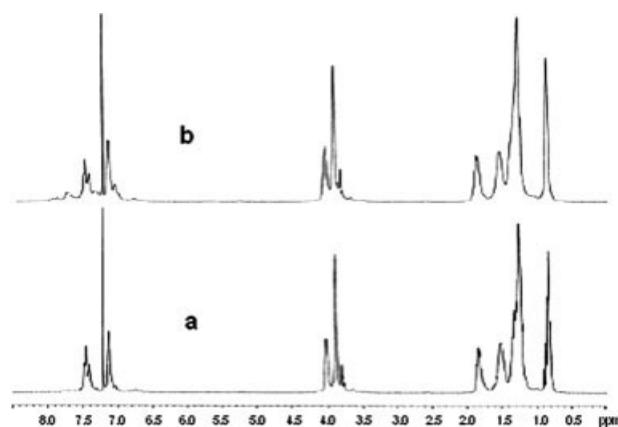


Figure 1 ¹H-NMR spectra: (a) PMOPV-BSeV0.5, (b) PMOPV-BSeV5.

TABLE II
UV-vis Absorption and Electrochemical Properties of the Copolymers in Solid State Films

Copolymers	$\lambda(\text{abs})_{\text{max}}$ (nm)	Optical band gap (eV) ^a	E_{ox} (V)	E_{red} (V)	HOMO (eV) ^b	LUMO (eV) ^b
PMOPV	485	2.12 (585)	0.55	-1.58	-4.95	-2.82
PMOPV-BSeV0.5	498	-	0.55	-1.54	-4.95	-2.86
PMOPV-BSeV1	497	-	0.55	-1.54	-4.95	-2.86
PMOPV-BSeV5	485	1.72 (720)	0.55	-1.52	-4.95	-2.88
PMOPV-BSeV15	466	1.72 (723)	0.55	-1.46	-4.95	-2.94
PMOPV-BSeV30	440/560	1.70 (729)	0.55	-1.40	-4.95	-3.00

^a Estimated from the onset wavelength of optical absorption in solid-state film. Values given in parentheses are λ_{onset} in nm.

^b Calculated from oxidation and reduction potential.

PL properties

The PL spectra of the copolymers in the solid films [Fig. 3(a)], including PL spectra of PMOPV for comparison, were taken under an excitation of a 488-nm line of Argon ion laser. The PL spectra in the solid films of all copolymers are dominated by the emission at a long wavelength region responsible for BSeV unit in the copolymers. Although the weak PL emission peak at about 585 nm of MOPV segments can be observed for copolymers with low BSeV content (0.5 and 1%), dominance of the BSeV long wavelength emission indicates that the energy transfer from the excitons created on the MOPV segment to the BSeV unit is highly efficient. The PL emission peaks are significantly red-shifted with increasing BSeV content in the copolymers (Table III). Since no large red shift was observed for absorption spectra of the corresponding copolymers (Fig. 2), the significant red shift in PL emission indicates that the Stokes shift increases with the increase of the BSeV content in the copolymers, which was observed previously in other PPV copolymers with narrow band-gap units in the main chain.^{12,13}

The PL spectra in chloroform solution of the copolymers were taken under an excitation of 488 nm line of Argon ion laser to investigate the energy transfer from the MOPV segment to the BSeV unit. Figure 3(b) shows the PL spectra of PMOPV-BSeV of all compositions in chloroform solution with a concentration of 1×10^{-3} mol/L (repeat unit). At this concentration, except copolymers with low BSeV content: PMOPV-BSeV0.5 and PMOPV-BSeV1, the PL spectra of copolymers are dominated by the long wavelength emissions at 700–760 nm with 5–30 mol % content of BSeV unit. For the copolymers with 0.5% BSeV content the emission peak is dominated by MOPV emission peaked at about 585 nm. When BSeV content increases to 1%, the intensity of BSeV emission increases greatly and the emission peak is the superposition of two compositions of almost equal intensity. When BSeV content increases to 5% and over, MOPV emission was completely quenched at this concentration (1×10^{-3} mol/L).

Figure 3(c) compares the PL spectra of PMOPV-BSeV5 in chloroform solution of different concentrations. It can be seen that relative intensity of PMOV and BSeV emissions changed with solution concentration. At dilute concentration (1×10^{-5} mol/L), significant intensity of PMOPV emission can be observed. When

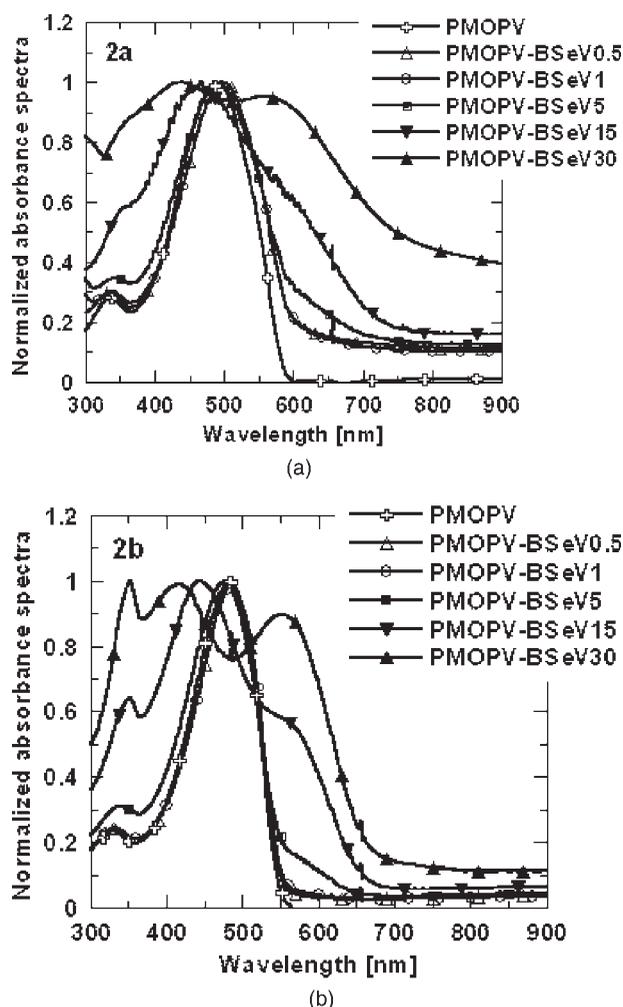


Figure 2 UV-vis absorption spectra of the copolymers: (a) PMOPV-BSeV in thin films, (b) PMOPV-BSeV in the chloroform solution (5×10^{-5} mol/L).

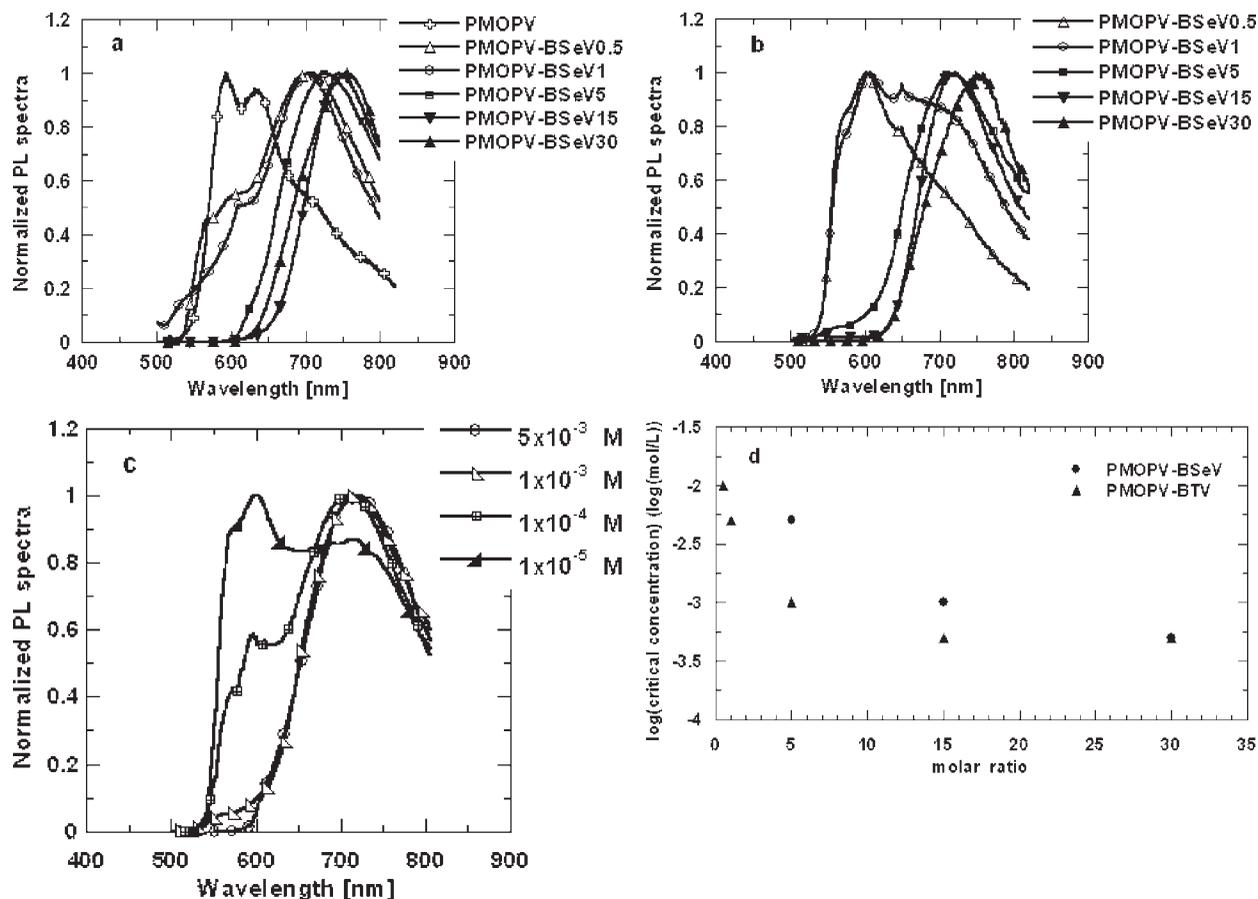


Figure 3 (a) PL spectra of the copolymers in thin films, (b) PL spectra of the copolymers in solution (1×10^{-3} M in chloroform), (c) PL spectra of PMOPV-BSeV5 in chloroform solution of different concentration, (d) Critical concentration (in log scale) defined as the concentration at which the MOPV emission is completely quenched versus molar ratio of BSeV or BTV (Ref. 12) in the copolymers.

solution concentration increases to 5×10^{-3} mol/L, the MOPV emission for PMOPV-BSeV5 is completely quenched. We define a critical concentration as the one at which the emission of host segment disappears completely. The critical concentration versus BSeV content of the copolymers is outlined in Figure 3(d). For comparison, the critical concentration versus BTV content of PMOPV-BTV (poly(2-methoxy-5-octyloxy-*p*-

phenylenevinylene-2,1,3-benzothiadiazolevinylene)¹² are also included in Figure 3(d). For both copolymers, the critical concentration decreases very quickly with increasing the narrow band-gap content. At low BSeV content, critical concentration of PMOPV-BSeV needs much higher concentration to get complete quenching PMOPV emission. It seems that the interchain interaction in PMOPV-BSeV copolymers is much weaker than

TABLE III
Absolute PL Efficiencies Measured in the Integrating Sphere

Copolymers	$\lambda(\text{PL})_{\text{max}}$ (nm)	Q(PL) _{max} (%)	PL properties of PMOPV-BTV of same composition ^a	
			$\lambda(\text{PL})_{\text{max}}$ (nm)	Q(PL) _{max} (%)
PMOPV	585	11.7	–	–
PMOPV-BSeV0.5	706	8.6	660	10.5
PMOPV-BSeV1	702	10.3	665	14.6
PMOPV-BSeV5	725	4.2	708	5.2
PMOPV-BSeV15	745	1.5	718	1.4
PMOPV-BSeV30	755	0.4	722	0.1

^a Taken from Ref. 12.

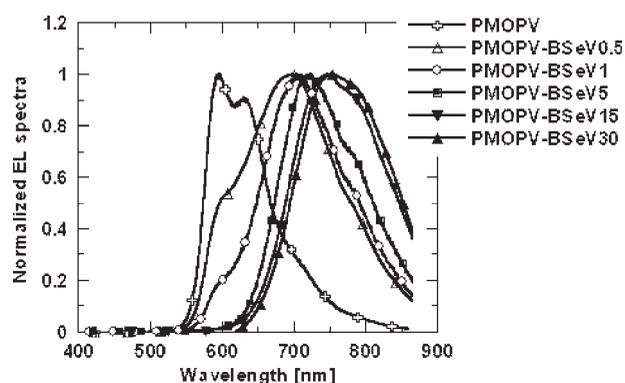


Figure 4 EL spectra of the copolymers.

that for PMOPV-BTV copolymers, for the atomic size of Se is greater than that of S.

The absolute PL efficiencies measured in the integrating sphere are listed in Table III. The PL efficiencies do not change dramatically by the incorporation of small number of BSeV units (0.5 and 1%). With the further increase of BSeV content up to 5% or more, the PL efficiencies start to decrease dramatically, which is probably due to the heavy atom quenching effect of Se. It is also interesting to compare photophysical properties of PMOPV-BSeV and PMOPV-BTV. Since the band gap of BSeV (Table II and Ref. 12) is narrower than that of BTV,³ the PL spectra of PMOPV-BSeV are 20–50 nm more red-shifted than those of PMOPV-BTV.¹² The absolute PL efficiency of PMOPV-BSeV is slightly lower than that of PMOPV-BTV of the same composition at low content of narrow band-gap units as listed in Table III where PL efficiency of PMOPV-BTV is shown for comparison.

EL properties

EL spectra of devices based on PMOPV and the copolymers in our standard device configuration (ITO/PEDOT : PSS/polymer/Ba/Al) are outlined in Figure 4, and the device performance is listed in

Table IV. Similar to PL spectra [Fig. 3(a)], EL emissions of the copolymers with BSeV content of 0.5 and 1% show a weak shoulder at around 590 nm responsible for PMOPV emission. The emission of MOPV is completely quenched only for the copolymers with BSeV content equal or greater than 5%. This is quite different from other intraenergy transfer polymers where EL emission always shows very different spectra compared with PL spectra of same composition at low doping concentration.^{3,12,13} The EL emission peaks of the copolymers are significantly red-shifted with increasing BSeV content. The copolymers with low BSeV content emit saturated red light, while the copolymers with higher BSeV content are red-shifted to NIR region. Compared with EL emission of their S-analogues, PMOPV-BTV of the same composition,¹² EL-emission peaks of PMOPV-BSeV are red-shifted around 20–40 nm. The EL-emission of PMOPV-BSeV30 peaks at 752 nm and is among the longest in the PPV polymers.¹³ With increasing the BSeV content, the QE_{ext} of PMOPV-BSeV devices first increases, and then decreases due to the concentration quenching effect of heavy Se atom, which is similar to the QE_{ext} of PMOPV-BTV.¹² The best device performance of the copolymers is observed for PMOPV-BSeV1 with the QE_{ext} of 0.26% and with CIE coordinate (0.65, 0.34). Although the preliminary device efficiency is rather low, device optimization is in progress and will be reported in forthcoming papers.

CONCLUSIONS

In conclusion, a series of novel conjugated PPV copolymers containing the phenylenevinylene segment and the benzoselenadiazole unit has been prepared by Stille cross-coupling reaction. The efficient energy transfer due to exciton trapping on the BSeV site has been observed. The EL emission peaks of the copolymers are significantly red-shifted with increasing BSeV content. The copolymers emit saturated-red to NIR light. The best performance of the preliminary

TABLE IV
Device Performance of the Copolymers

Copolymers	$\lambda_{(\text{EL})\text{max}}$ (nm) ^a	Bias (V) ^b	I^c (mA/cm ²)	B^d (cd/m ²)	QE_{ext}^e (%)
PMOPV	591	5.5	35.5	61	0.17
PMOPV-BSeV0.5	700	11.2	42.0	25	0.12
PMOPV-BSeV1	705	11.4	48.0	21	0.26
PMOPV-BSeV5	724	11.0	25.0	17	0.10
PMOPV-BSeV15	746	7.4	21.0	9	0.05
PMOPV-BSeV30	752	4.6	10.0	3	0.02

^a Maximum EL emission wavelength.

^b Operating voltage at maximum luminance.

^c Current density at maximum luminance.

^d Maximum luminance.

^e Maximum external quantum efficiency.

devices composed of the copolymers with 1% content of BSeV units is observed.

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