Pure Blue Electroluminescent Poly(aryl ether)s with Dopant–Host Systems

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ABSTRACT: A series of novel arylene ether polymers (P5F-BCzVFs) containing both pentafluorene (5F) and distyrylarylene derivative (BCzVF) units in the side chains for efficient pure blue light emission were prepared by a facile, metal-free condensation polymerization. The emission spectra indicated that color tuning could be achieved through efficient Förster energy transfer from the deep-blue 5F host to the pure-blue BCzVF dopant. Single-layer polymer light-emitting diodes (PLEDs) based on P5F-BCzVFs (ITO/(PEDOT:PSS)/polymer/Ca/AI) exhibited voltage-independent and stable pure blue emission with a Commission International de L'Eclairage (CIE) coordinate of

INTRODUCTION Polymer light-emitting diodes (PLEDs) have attracted much attention because of their potential application in the large-area, flat-panel display field.¹⁻¹² For fullcolor display, blue, green, and red fluorophores with high emission efficiency and high color purity are required. In particular, blue light-emitting polymers are essential as blue light sources for PLEDs or polymer hosts for green and red dopants.^{13,14} Most of research about blue light-emitting polymers focused on fluorene-based polymers, owing to their high photoluminescence (PL) efficiency and wide bandgap.^{15–22} Nevertheless, low electroluminescence (EL) device efficiency and poor EL color stability during device operation hamper their further application.²³⁻²⁶ Moreover, the human eyes is not very sensitive to the deep blue emission of typical polyfluorenes (415 nm).^{27,28}

Development of EL polymers with dopant-host systems have been proved to be a successful strategy to tune colors and to enhance the efficiency and stability of PLEDs.^{29–33} In most cases, polyfluorene were used as the host material, and highly efficient red, green, and sky blue EL polymers have been reported.^{34–38} However, very few works are about pure blue emission EL polymers.^{39–41} Shu and coworkers³⁹ reported a (0.15, 0.15), a maximum brightness of 3576 cd/m², and a maximum luminous efficiencies of 2.15 cd/A, respectively. As most polymers with dopant-host systems, the luminous efficiencies of all P5F-BCzVFs surpassed that of the host-only polymer (P5F), due to the energy transfer and charge trapping from the host to the dopant. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3911–3919, 2011

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polyfluorene derivative that contain bis(2,2-diphenylvinyl) fluorene as a pendant with a maximum external quantum efficiency of 1.06% with color coordinates of (0.15, 0.17). A polyfluorene derivative that contains 1 mol % 2-hexylbenzotriazole (HBT) in the main chain has been reported by Cao et al.⁴⁰ and its PLED exhibited a luminance efficiency of 2.69 cd/A with a color coordinate of (0.15, 0.17). Our group reported a series of blue polyfluorene derivatives of dopant-host systems and their single-layer PLEDs with the luminance efficiency of 3.43 cd/A, the maximum brightness of 6539 cd/m², and CIE coordinates of (0.15, 0.16).⁴¹

However, most of these blue-emission polymers polymerized by expensive transition metal catalysts, and the removing of the residual catalysts is still a great challenge.^{42,43} In previous works, our group have reported novel poly(aryl ether)s (PAEs) with pentafluorene (5F) in the side chains (P5F), which exhibited the similar EL performance with polyfluorenes.⁴⁴ In this article, we report a series of pure blue poly (aryl ether)s (P5F-BCzVFs) containing dopant/host systems by a traditional condensation reaction without any metal catalysts. Pentafluorene (5F) and distyrylarylene derivative (BCzVF) units are attached orthogonally to the main chains of the polymers as pendant

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SCHEME 1 Synthesis of poly(aryl ether)s. (i) *n*-BuLi, DMF, THF; (ii) LiAlH₄, THF; (iii) CBr₄, PPh₃, THF; (iv) P(OEt)₃, reflux; (v) NaOH (50% aq), bromoethane, Tetrabutylammonium bromide, toluene; (vi) DMF, POCl₃; (vii) t-BuOK, THF; (viii) K₂CO₃, toluene, DMAc, 140 °C and then 170 °C.

groups (Scheme 1). Poly(aryl ether) was selected as the polymer skeleton due to the ease of synthesis and purification and also because of its high thermal stability, and excellent film formation capability.⁴⁵ Effective energy transfer from the deep blue pentafluorene units to the pure blue BCzVF units may occur, leading to their emission predominantly from BCzVF. The pure blue emission at 445 nm is more sensitive for human eyes than that of polyfluorenes. In addition, the orthogonally connect style between pendant groups and the main chains of poly(aryl ether)s induce a big steric hindrance that can reduce the π - π stacking and depress the crystalline tendency of polymers, which may result in stable and efficient blue electroluminescence.

EXPERIMENTAL

Material

Dimethylacetamide (DMAc) were dried and distilled from finely powdered calcium hydride. Tetrahydrofuran (THF) and toluene were distilled over sodium/ benzophenone. 2,7-Dibromo-9,9-bis(4-fluoro-3-(trifluoromethyl)phenyl)fluorine and monomer 5F were synthesized as previously described.⁴⁴ All other reagents and solvents were used as received from commercial sources without further purification.

9,9-Bis(4-fluoro-3-(trifluoromethyl)phenyl)fluorine-2,7dicarbaldehyde (1)

To a solution of 2,7-dibromo-9,9-bis(4-fluoro-3-(trifluoromethyl)phenyl)fluorine (6g, 9.3 mmol) in anhydrous THF (250 mL) was slowly added *n*-BuLi (8.9 mL,2.5 M in hexane, 22.2 mmol) at -78 °C. The mixture was stirred at -78 °C for 2 h. *N*,*N*-Dimethylformamide (DMF) (4 mL) was added to the solution, and the resulting mixture was stirred at -78 °C for 1 h, warmed to room temperature and stirred overnight followed by quenching with 250 mL of HCl (2.0 M). After extraction with dichloromethane three times, dried over anhydrous Na₂SO₄. Solid residues collected by evaporating off the solvent were purified by column chromatography on silica gel to afford the target compound with a yield of 75%. ¹H NMR (300 MHz, CDCl₃): δ 8.08 (d, 2H, J = 7.9 Hz), 8.03 (dd, 2H, J = 7.9 Hz, 1.2 Hz), 7.85 (s, 2H), 7.46–7.41 (m, 2H), 7.28 (dd, 2H, J = 6.4 Hz, 2.3 Hz), 7.18 (t, 2H, J = 9.2 Hz).

2,7-Bis(bromomethyl)-9,9-bis(4-fluoro-3-(trifluoromethyl)phenyl)fluorine (3)

The solution of lithium aluminium hydride (4.5 mmol) in THF was added dropwise to a solution of 9,9-Bis(4-fluoro-3-(trifluoromethyl)phenyl)fluorine-2,7-dicarbaldehyde (7.5)mmol) in THF (150 mL). The resulting mixture was stirred at room temperature for 1 h. Then the mixture was poured into water slowly and extracted with diethyl ether. The organic extracts were dried with anhydrous Na₂SO₄. After the solvent had been removed, the crude compound 2 was dissolved in THF, then tetrabromomethane (CBr₄) (9.3 mmol) and triphenylphosphine (PPh₃) (9.3 mmol) was added quickly at room temperature. After the addition was complete, the mixture was stirred for1h at room temperature and then added dichloromethane and water. The organic layer was extracted with dichloromethane, and the combined organic layers were dried with Na₂SO₄. After the solvent had been removed by rotary evaporation, the residue was purified by column chromatography on silica gel to give the target compound 3. Yield: 88%.

¹H NMR (300 MHz, CDCl₃): δ 7.91 (d, 2H, J = 10.7 Hz), 7.59–7.54 (m, 2H), 7.42 (s, 2H), 7.41 (d, 2H, J = 8.1 Hz), 7.30 (dd, 2H, J = 6.7 Hz, 2 Hz), 4.50 (d, 2H, J = 5.4 Hz).

2,7-Bis(diethoxyphosphorylmethyl)-9,9-bis (4-fluoro-3-(trifluoromethyl)phenyl)fluorine (4)

A mixture of **3** (3.7 mmol) and triethyl phosphate (5 mL) was heated at 150 $^{\circ}$ C for 15 h. Excess triethyl phosphite was evaporated under vacuum, and the residue was added to hexane. The precipitate was purified by column chromatography on silica gel with ethyl acetate to give the target compound **4**. Yield: 97%.

¹H NMR (300 MHz, CDCl₃): δ 7.66 (d, 2H, J = 7.8 Hz), 7.36–7.20 (m, 6H), 7.05 (t, 2H, J = 9 Hz), 3.94–3.74 (m, 8H), 3.06 (d, 2H, J = 21.6 Hz), 1.04 (t, 12H, J = 7.2 Hz).

N-Ethylcarbazole (5)

A mixture of carbazole (42 mmol), toluene (40 mL), 50% of the sodium hydroxide solution (25 mL), bromoethane (48 mmol) and Tetrabutylammonium bromide (0.5 g) was heated under reflux for 16 h, cooled and extracted with dichloromethane. The combined organic layers were dried with Na₂SO₄. After the solvent had been removed by rotary evaporation, the residue was purified by column chromatography on silica gel to give the target compound. Yield: 90%.

¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, 2H, J = 7.6 Hz), 7.58 (t, 2H, J = 7.6 Hz), 7.50 (d, 2H, J = 8.4 Hz), 7.35 (t, 2H, J = 7.6 Hz), 4.37 (q, 4H, J = 9.3 Hz), 1.45 (t, 6H, J = 7.2 Hz).

N-Ethyl-3-aldehyde Carbazole (6)

To a stirred solution of *N*-ethylcarbazole (30 mmol) of 50 mL *N*,*N*-Dimethylformamide was added dropwise 7 mL (75 mmol) of phosphorusoxychloride (POCl₃) at 0 °C for 30 min, then enhanced to 98 °C for extra 2 h. Then the mixture was

cooled to room temperature, extracted with dichloromethane, and then combined organic layers were dried with Na_2SO_4 . After the solvent had been removed by rotary evaporation, the residue was purified by column chromatography on silica gel to give the target compound. Yield: 84%.

¹H NMR (400 MHz, CDCl₃): δ 10.09 (s, 1H), 8.60 (s, 1H), 8.15 (d, 1H, J = 7.6 Hz), 8.00 (dd, 1H, J = 8.8 Hz, 1.2 Hz), 7.53 (t, 1H, J = 7.2 Hz), 7.46 (d,1H, J = 5.6 Hz), 7.44 (d, 1H, J = 5.2 Hz), 7.32 (t, 1H, J = 7.6 Hz), 4.37 (q, 4H, J = 9.3 Hz), 1.45 (t, 6H, J = 7.2 Hz).

BCzVF

The solution of potassium tert-butoxide in anhydrous THF was dropped to a stirred solution of compound **4** and 9-ethyl-3-carbazolcarboxaldehyde in anhydrous THF under nitrogen at room temperature, then the mixture was heated under reflux for 6 h, cooled, and then dropped to water. The precipitate was purified by column chromatography to give the target compound with a yield of 60%.

¹H NMR (300 MHz, CDCl₃): δ 8.23 (s, 2H), 8.12 (d, 2H, J = 7.5 Hz), 7.79 (d, 2H, J = 7.8 Hz), 7.66 (d, 4H, J = 7.8 Hz), 7.51–7.37 (m, 12H), 7.25 (d, 4H, J = 9.3 Hz), 7.20–7.13 (m, 4H), 4.37 (q, 4H, J = 9.3 Hz), 1.45 (t, 6H, J = 7.2 Hz). MS (MALDI-TOF): m/z: 928.3[M⁺].

General Polymerization Procedure

To a mixture of 4,4'-dihydroxydiphenylpropane, 5F and BCzVF with a determined feed ratio, toluene (2 mL), DMAc (1.5 mL), and K_2CO_3 (0.58 g, 0.42 mmol) in a two-necked 20 mL glass reactor equipped with a Dean-Stark trap was heated to 140 °C for 3 h then enhanced to 170 °C for extra 24 h. Then the mixture was cooled to room temperature and diluted with 50 mL dichloromethane. The organic portion was washed with water, dried with anhydrous MgSO₄, and concentrated into 2 mL. The polymer was precipitated with methanol, followed by purification with Soxhlet extraction with acetone and precipitated into methanol twice. The resulting polymers are green or light-yellow solid with a yield of 70–80%.

P5F

Yield: 73%. ¹H NMR (400 MHz, CDCl₃): δ 7.87(d, 2H, *J* = 7.8 Hz), 7.78-7.60 (m, 24H),7.51-7.50 (m, 4H), 7.35-7.28 (m, 6H), 7.15 (d, 4H, *J* = 8.4 Hz), 6.91 (d, 4H, *J* = 8.4 Hz), 6.79-6.77 (m, 2H), 2.04-2.00 (m, 16H), 1.58 (s, 6H), 1.18-0.71 (m, 120H); Anal. Calcd: H, 8.49; C, 84.98; Found: H, 8.34; C, 84.62.

P5F-BCzVF1

Yield: 80%. ¹H NMR (400 MHz, CDCl₃): δ 8.21 (Ar—H, weak peak of BCzVF units), 8.11 (Ar—H, weak peaks of BCzVF units), 7.86 (Ar—H), 7.77-7.63 (Ar—H), 7.53 (Ar—H), 7.36-7.33 (Ar—H), 7.17 (Ar—H), 6.94 (Ar—H), 6.80 (Ar—H), 4.33 (m, CH₂ of BCzVF units), 2.05 (m, CH₂ of SF units), 1.61 (s, CH₃), 1.18-0.71(m, CH₂ and CH₃). Anal. Calcd: H, 8.49; C, 84.93. Found: H, 8.47; C, 84.96.

P5F-BCzVF3

Yield: 75%. ¹H NMR (400 MHz, $CDCl_3$): δ 8.22 (Ar—H, weak peak of BCzVF units), 8.11 (Ar—H, weak peaks of BCzVF



units), 7.87 (Ar—H), 7.78-7.64 (Ar—H), 7.54 (Ar—H), 7.36-7.33 (Ar—H), 7.17 (Ar—H), 6.94 (Ar—H), 6.80 (Ar—H), 4.33 (m, CH₂ of BCzVF units), 2.05 (m, CH₂ of 5F units), 1.61 (s, CH₃), 1.18-0.71 (m, CH₂ and CH₃). Anal. Calcd: H, 8.69; C, 84.46. Found: H, 8.43; C, 84.88.

P5F-BCzVF5

Yield: 72%. ¹H NMR (400 MHz, CDCl₃): δ 8.20 (Ar—H, weak peak of BCzVF units), 8.09 (Ar—H, weak peaks of BCzVF units), 7.86 (Ar—H), 7.77-7.62 (Ar—H), 7.51 (Ar—H), 7.36-7.28 (Ar—H), 7.14 (Ar—H), 6.92 (Ar—H), 6.78 (Ar—H), 4.31 (m, CH₂ of BCzVF units), 2.03 (m, CH₂ of 5F units), 1.59 (s, CH₃), 1.18-0.71 (m, CH₂ and CH₃). Anal. Calcd: H, 8.60; C, 84.92. Found: H, 8.40; C, 84.84.

P5F-BCzVF10

Yield: 71%. ¹H NMR (400 MHz, CDCl₃): δ 8.23 (Ar—H, weak peak of BCzVF units), 8.08 (Ar—H), weak peaks of BCzVF units), 7.86 (Ar—H), 7.77-7.62 (Ar—H), 7.51 (Ar—H), 7.36-7.30 (Ar—H), 7.14 (Ar—H), 6.92 (Ar—H), 6.78 (Ar—H), 4.31 (m, CH₂ of BCzVF units), 2.02 (m, CH₂ of 5F units), 1.59 (s, CH₃), 1.18-0.72 (m, CH₂ and CH₃). Anal. Calcd: H, 8.25; C, 84.83. Found: H, 8.31; C, 84.72.

Measurement and Characterization

¹H NMR spectra were recorded on a Bruker AV300 or AV400 NMR spectrometer. Mass spectra were obtained on a LDI-1700 matrix-assisted laser desorption/ionization timeof-flight (MALDI TOF) mass spectrometer (American Linear Scientific). Gel permeation chromatography (GPC) was performed by a Waters 410 instrument with polystyrene as standard and THF as eluent. The elemental analysis was performed using a Bio-Radele mental analysis system. The UV/ vis absorption and PL spectra were obtained on a Perkin-Elmer Lambda 35 UV/vis spectrometer and a Perkin-Elmer LS50B luminescence spectrometer, respectively. The cyclic voltammetry was recorded on an EG&G model 283 potentiostat/galvanostat system at room temperature using a Ag/ AgCl electrode as the reference electrode, a platinum wire as the auxiliary electrode, and a platinum plate as the working electrode in acetonitrile solution of $(n-Bu)_4 NClO_4$ (0.1 M) with the scan rate of 100 mV/s. Thermal properties of the polymers were obtained using Perkin-Elmer DSC7 and TGA7 equipment at a heating/cooling rate of 10 °C/min under a nitrogen atmosphere.

Device Fabrication and Characterization

PLEDs were fabricated with a configuration of ITO/ PEDOT:PSS/polymers/Ca/Al. The poly(styrene sulfonic acid) doped poly(ethylenedioxythiophene) (PEDOT:PSS) layer was spin-coated directly onto the cleaned ITO at 3000 rpm for 60 s and then baked for 30 min at 120 °C to give an approximate thickness of 50 nm. Then the polymer layer (~100 nm) was spin-coated on to the PEDOT:PSS/ITO coated glass substrate in fresh toluene solution (20 mg/mL) under ambient atmosphere. Finally a 10 nm thick calcium layer and a 100 nm thick aluminum layer were deposited by thermal sublimation under a vacuum level of 10^{-4} Torr. The electroluminescence (EL) spectra and current-voltage and brightness-voltage curves of devices were measured under ambi-

TABLE 1 Molecular Weights and Thermal Properties of Polymers

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Polymer	$\mathit{M}_{ m n} imes 10^{4a}$	$M_{ m w} imes$ 10 ^{4a}	PDI	$T_{d} (^{\circ}C)^{b}$
P5F	10.2	23.8	2.3	424
P5F-BCzVF1	4.0	7.3	1.8	416
P5F-BCzVF3	3.9	5.8	1.5	415
P5F-BCzVF5	2.0	3.7	1.8	423
P5F-BCzVF10	4.4	7.0	1.6	418

^a Molecular weights were determined by GPC, eluting with THF, by comparison with polystyrene standards.

 $^{\rm b}$ Temperature at which a 5% weight loss occurred was determined at a heating rate of 10 $^\circ C$ /min under a nitrogen atmosphere.

ent conditions using a Keithley 2400/2000 current/voltage source unit with a calibrated silicon photodiode.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polymers

The synthesis of monomers and polymers are illustrated in Scheme 1. Compound 4 was synthesized with a total yield more than 60% beginning from 2,7-Dibromo-9,9-bis(4-fluoro-3-(trifluoromethyl)-phenyl)fluorene. The monomers BCzVF was synthesized by Horner-Emmons coupling reaction in a yield of 60%. All the polymers were synthesized by the nucleophilic displacement reaction as the traditional PAEs. Compared with the Suzuki or Yamamoto coupling reactions, their purification process is very simple, and there is no need to use chromatography or other special techniques to remove metal catalyst residues. As shown in Scheme 1, 5F and BCzVF were attached to the main chains of poly(aryl ether)s through two phenyl rings at the 9-position of the central fluorene unit. Due to the sp^3 characteristic of the bridge carbon (9-position) of fluorene, all fluorophores locate nearly orthogonally to the poly(aryl ether)s main chain, and the main chain of poly(aryl ether)s primarily serves as a skeleton, and the optical properties mainly depend on the side chains. The orthogonally linkage also leads to a big steric hindrance that will reduce the π - π stacking of polymer chains and depressing the crystalline tendency of polymers. The monomer molar feed ratios of the BCzVF units to the pentafluorene units are 0:100, 1:100, 3:100, 5:100, and 10:100, and the corresponding polymers are referred to as P5F, P5F-BCzVF1, P5F-BCzVF3, P5F-BCzVF5, and P5F-BCzVF10, respectively. The actual ratios of the BCzVF units to 5F units in the resulting polymers were estimated by ¹H NMR spectra and the results are in good agreement with the monomer feed ratios.

Gel permeation chromatography (GPC) revealed the weightaverage molecular weight (M_w) of (3.7–23.8) × 10⁴ with polydispersities (M_w/M_n) of 1.5–2.3 for the five polymers as shown in Table 1. The thermal properties of these five copolymers by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were investigated with a scan rate of 10 °C/min under nitrogen atmosphere. As shown in Figure 1 and Table 1, all polymers are thermally



FIGURE 1 TGA curves of the polymers P5F, P5F-BCzVF1, P5F-BCzVF3, P5F-BCzVF5, P5F-BCzVF10.

stable and have the onset decomposition temperatures (T_d) of about 420 °C in N₂. DSC data indicate that the polymer P5F exhibits a glass transition temperature at 84 °C, which is higher than that of poly(9,9-dicotylfluorene) (75 °C).⁴⁶ We did not find any phase transition signals during repeated heating/cooling DSC cycles for P5F-BCzVFs from room temperature to 300 °C. In addition, all the polymers are soluble in common solvents such as dichloromethane, chloroform, toluene, and tetrahydrofuran.

Optical Properties

The absorption and PL spectra of the monomers are shown in Figure 2, and the spectral data are summarized in Table 2. In toluene solution, 5F and BCzVF exhibited the absorption maxima at 370 and 405 nm, respectively. The PL emission peak of BCzVF spectrum is at 445 nm while 5F's emission peak is at 413 nm. The full width at half-maximum (FWHM) value of BCzVF is only about 49 nm, and the PL quantum yields of BCzVF is 0.59 relative to 9,10-diphenylanthracene in cyclohexane ($\Phi_f = 0.9$). In addition, as shown in Figure 2, the emission spectrum of 5F and the absorption spectrum of BCzVF display a good overlap, which will facilitate efficient energy transfer from 5F to BCzVF.



FIGURE 2 Normalized absorption and PL spectra of 5F and BCzVF in toluene.

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FIGURE 3 Normalized absorption and PL spectra of the poly-

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TABLE 2 Optical Properties of Compounds 5F and BCzVF

Compound	λ _{abs, max} (nm) ^a	λ _{PL, max} (nm) ^a	Ф _{FL} (%) ^b	FWHM (nm) ^c
ōF	370	413 (436)	95	48
BCzVF	405 (425)	445 (472)	59	49

 $^{\rm a}$ Solution spectra were measured in toluene with a concentration of $10^{-5}~\text{M}.$

 b Fluorescence quantum efficiency ($\Phi_{FL})$ was measured in toluene with a concentration of 10^{-7} M and 9,10-diphenylanthracene ($\Phi=$ 0.9) as the standard.

^c Full width at half-maximum.

Figure 3 presents the absorption spectra and PL spectra of P5F-BCzVFs in toluene solution. The absorption spectra of P5F-BCzVFs are identical to P5F, which demonstrate that the absorption of all the polymers mainly originate from the absorption of 5F units, perhaps due to the low amounts of BCzVF units in the polymers. The PL spectra of P5F-BCzVFs in solution show that incomplete energy transfer happened from the 5F units to BCzVF units. With increasing BCzVF content in P5F-BCzVFs, the relative intensity of the deep blue emission from 5F becomes weaker gradually, and the emission peak is red-shifted as well.

The absorption spectra of P5F-BCzVFs in film (Fig. 4) are similar to those in solution (Table 3). Unlike their toluene solutions, even for P5F-BCzVF1, the intensity of the emission from 5F is already suppressed significantly in thin film. These results clearly indicate that much more efficient Förster energy transfer happen in film compared to dilute solution. With the increasing of BCzVF content, the emission from 5F units is quenched completely, and their PL spectra are similar to that of BCzVF, suggesting that the PL emission of P5F-BCzVFs in thin film is majorly from BCzVF.

We also studied spectral stability of P5F-BCzVFs after thermal annealing at 200 °C under vacuum for 10 h. As shown in Figure 5, different from polyfluorene,⁴⁷ the PL spectra of P5F-BCzVFs are almost same before and after thermal annealing, indicating their excellent spectral stability.



FIGURE 4 Normalized absorption and PL spectra of the polymers in the solid state.

Electrochemical Properties

The electrochemical properties of monomers 5F and BCzVF were investigated by means of cyclic voltammetry (CV) with a typical three-electrode cell using ferrocene as the internal standard (Fig. 6). From the onset oxidation and reduction potentials in the cyclic voltammogram, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the monomers can be estimated. 5F and BCzVF show the HOMO levels of -5.8 and -5.5 eV, LUMO levels of -2.1 and -2.3 eV, respectively. We

TABLE 3 Optical Properties of the Polymers

	FW/HM	$\lambda_{abs, max} (nm)^{b}$		$\lambda_{PL,\ max}$ (nm) ^c	
Polymer	(nm) ^a	Solution	Film	Solution	Film
P5F	52	369	370	413 (435)	419 (442)
P5F-BCzVF1	55	370	370	413 (437)	443 (470)
P5F-BCzVF 3	58	370	370	415 (437)	449 (475)
P5F-BCzVF 5	60	370	370	439 (415)	449 (472)
P5F-BCzVF 10	59	370	370	442 (415)	449 (474)

^a Full width at half-maximum of PL spectra of the polymers in film.

^b Evaluated in 10⁻⁵ M toluene solution.

^c Prepared by spin-coating from a toluene solution.

further investigated the electrochemical behavior of the polymer thin films spin-coated on a glassy carbon electrode. The polymers show the similar electrochemical properties of 5F, perhaps also due to the low contents of BCzVF units. As shown in Figure 6, the LUMO and HOMO energy levels of BCzVF lie between those of 5F, suggesting favorable charge trapping of BCzVF units for P5F-BCzVF will happen in the EL process.⁴⁸

Electroluminescent Properties

The PLEDs based on P5F-BCzVFs were fabricated with a single-layer configuration of ITO/(PEDOT:PSS)/polymer/Ca/Al, and all the EL data are summarized in Table 4. As shown in Figure 7, the EL spectrum of the device based on P5F is



FIGURE 5 Normalized film-state PL spectra of the polymers before (solid) and after annealing at 200 °C for 10 h (dash) under vacuum.



FIGURE 6 LUMO and HOMO energy levels of 5F and BCzVF.

similar to its PL spectrum with the emission peak at 420 nm and the CIE coordinate (0.16, 0.10), which is also located in the deep blue region. With the increasing of BCzVF content, the EL spectra are red shifted gradually. Even for P5F-BCzVF1, the emission from 5F is nearly complete quenched due to efficient energy transfer. The EL emissions of P5F-BCzVF1, P5F-BCzVF3, and P5F-BCzVF5 exhibit blue emission peaks around 440-460 nm and their corresponding CIE coor-

dinates fall in the pure blue region. In addition, they show narrow EL spectra with the FWHM smaller than 60 nm, indicating their excellent color purity. Moreover, their EL spectra are voltage-independent. Taking P5F-BCzVF3 as an example, its EL spectra are very stable with the same CIE coordinates of (0.15, 0.15) from 6 to 10 V (Fig. 8). For P5F-BCzVF10, its emission peak is at 479 nm with the corresponding CIE coordinate at (0.16, 0.21), which even deviated from the pure blue region.

The luminous efficiency-current density curves of the polymers are shown in Figure 9. In comparison with the low luminous efficiency (0.61 cd/A) of P5F, P5F-BCzVF1, P5F-BCzVF3, P5F-BCzVF5, and P5F-BCzVF10 exhibit much higher luminous efficiencies up to 2.15 cd/A, demonstrating the advantage of dopant-host systems. The turn-on voltages are increased from 4.2 V to 5.5 V, with the increasing of BCzVF content in the polymers, perhaps due to the charge trapping of the dopant units.⁴⁹ The maximum brightness of all the P5F-BCzVFs devices was in the range of 2342-4035 cd/m², also much higher than that of the P5F device (875 cd/m^2). The enhanced performance of P5F-BCzVFs relative to P5F should be attributed to both the energy transfer and the charge trapping from the 5F host to the BCzVF dopant as other highly efficient EL polymers with dopant-host systems. Among these P5F-BCzVF copolymers, the device based on P5F-BCzVF3 (Fig. 10) is the best one, which emits pure blue

TABLE 4 EL Performance Data of the Devices with the Configuration of ITO/PEDOT: PSS/Polymer/Ca/Al

Polymer	$\lambda_{EL, max}$ (nm)	$V_{\rm on}^{\ a}$ (V)	$L_{\rm max}^{\rm b}$ (cd/m ²)	LE _{max} ^c (cd/A)	CIE (x, y)	FWHM ^d (nm)
P5F	420 (442)	4.4	875	0.61	0.16, 0.10	48
P5F-BCzVF1	445 (470)	4.2	2472	1.66	0.15, 0.12	49
P5F-BCzVF3	447 (471)	4.2	3576	2.15	0.15, 0.15	54
P5F-BCzVF5	448 (476)	5.0	2342	1.99	0.15, 0.16	57
P5F-BCzVF10	479 (453)	5.5	4035	1.44	0.16, 0.21	63

^a Onset voltage at the brightness of 1 cd/m².

^b Maximum brightness.

^c Maximum luminous efficiency.

^d Full width at half-maximum.



FIGURE 7 Normalized EL spectra of the polymers.



FIGURE 8 Normalized EL spectra of ITO/PEDOT/P5F-BCzVF3/Ca/ Al at different voltages.



FIGURE 9 Current density-luminous efficiency curves of the devices based on the polymers.



FIGURE 10 Voltage-brightness-current density plots of the device based on the polymer P5F-BCzVF3.

light with the CIE coordinates (0.15, 0.15), a remarkable maximum brightness of 3576 cd/m², a luminous efficiency up to 2.15 cd/A.

CONCLUSIONS

In summary, we have designed and synthesized a series of novel poly(aryl ether)s (P5F-BCzVFs) with dopant-host systems containing pentafluorene as the host and BCzVF as the dopant by a facile, metal-free condensation polymerization. The PL spectra of the polymers in film indicated that color tuning can be realized through efficient energy transfer from pentafluorene to BCzVF. And all the polymers showed good emission color stability even after annealing at 200 °C under vacuum for 10 h. Their EL emission peaks are located around 440–460 nm with a narrow FWHM below 60 nm, both of which endowed these poly(aryl ether)s with sensitive blue emissions to human eyes and good color purity. In comparison with P5F, the luminous efficiencies of the EL devices based on P5F-BCzVF3 are significantly improved. The devices based on P5F-BCzVF3 exhibit pure blue emissions with the CIE coordinates of (0.15, 0.15), a maximum luminous efficiency of 2.15 cd/A, and a maximum brightness of 3576 cd/m². In addition, the EL spectra of P5F-BCzVFs exhibit good color stability at different voltage. All of these results demonstrate that these highly efficient, color-stable, pure blue emissive poly(aryl ether)s are promising candidates for blue EL polymers.

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