# Synthesis, Characterization, and Electroluminescence Properties of Poly(fluorenevinylene benzobisthiazoles)

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ABSTRACT: A series of vinylene-linked copolymers based on electron-deficient benzobisthiazole and electron-rich fluorene moieties were synthesized via Horner–Wadsworth–Emmons polymerization. Three different polymers **P1**, **P2**, and **P3**, were prepared bearing octyl, 3,7-dimethyloctyl, and 2-(2-ethoxy)ethoxyethyl side chains, respectively. The polymers all possessed moderate molecular weights, good solubility in aprotic organic solvents, and high fluorescence quantum efficiencies in dilute solutions. **P2**, which bore branched 3,7-dimethyloctyl side chains, exhibited better solubility than the other polymers, but also exhibited the lowest thermal decomposition temperature of all

**INTRODUCTION** Conjugated polymers are currently of interest due to their potential impact on a diverse range of technologies, including polymer light-emitting diodes (PLED)s,<sup>1</sup> organic photovoltaic cells<sup>2</sup> and field-effect transistors (FETs).<sup>3</sup> Research in this area is motivated by the opportunity to fabricate large area displays via low-cost solution processing techniques and tuning of the optical properties of the polymers through chemical synthesis. Since the discovery of electroluminescence in poly(phenylene vinylene), poly (arylene vinylene)s (PAVs) have been widely studied for the development of emissive polymers. The incorporation of vinylene linkages into the polymer backbone is advantageous as they reduce torsional interactions between adjacent rings, which increases planarization and effective conjugation length, as well as reduces ionization potentials (IPs) and hole injection barriers. <sup>4</sup> Vinylene groups also increase the rotational flexibility of the polymer chain, which can enhance polymer solubility.<sup>5</sup> The properties of PAVs can be further modified by the incorporation of electron-deficient heterocycles into the polymer backbone to increase the polymers' electron affinity.<sup>6</sup> Accordingly, the synthesis of PAVs comprising electron-deficient heterocycles has been investigated for

polymers. Overall, the impact of the side chains on the polymers optical properties in solution was negligible as all three polymers gave similar absorption and emission spectra in both solution and film. Guest-host light-emitting diodes using dilute blends of the polymers in a poly(*N*-vinylcarbazole) host gave blue-green emission with **P2** exhibiting the highest luminous efficiency, 0.61 Cd/A at ~500 nm. © 2012 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 916–923

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the development of emissive materials with better charge injection and transport properties.  $^{6(d),7}$ 

Among electron-deficient heterocycles, benzobisthiazole is unique as it contains two sulfur atoms and two nitrogen atoms within its fused three-ring system. Benzobisthiazole polymers and small molecules have been used as organic semiconductors in a variety of applications, including nonlinear optical materials,<sup>8</sup> FETs,<sup>9</sup> light-emitting diodes (LEDs),<sup>10</sup> and photovoltaic cells.<sup>9(a-c),11</sup> When used as electron-transport layers, polybenzobisthiazoles improved the performance of PAV based LEDs.<sup>10(b)</sup> When used as emissive materials, thin films of poly(benzobisthiazo1e-1,4-phenylenebisvinylene) emitted red light with an emission peak at 640 nm and an estimated quantum yield of  $4\text{--}5\%.^{10(a)}$  In spite of their many beneficial qualities, the development of benzobisthiazole-containing materials has been hindered by two factors: the poor solubility of the resulting polymer, requiring processing from strongly acidic solutions; and harsh reaction conditions for their synthesis, which limit the types of substituents that can be incorporated into the polymer backbone. However, the recent development of monomers based on functional benzobisthiazoles has

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created the opportunity to develop new PAVs based on this moiety.  $^{12} \$ 

In this article, we report the synthesis, characterization, and electroluminescent properties of three new PAVs composed of fluorene and benzobisthiazole. We used 9,9-dialkylfluorenes as comonomers as they have been widely utilized in the synthesis of electroluminescent polymers. In general fluorene-based polymers have excellent solubility, high solidstate photoluminescence (PL) quantum yield and good charge carrier mobility.<sup>13</sup> Unfortunately, many fluorenecontaining polymers have low electron affinities and high IPs, which makes the charge carrier injection difficult.7(a),13,14 Previously, we synthesized poly(fluorene vinylene-alt-benzobisoxazole)s, which exhibited reversible reduction processes and stable blue emission with luminous efficiencies of up to 1 Cd/A at  $\sim$ 470 nm in guest-host PLEDs using a poly(N-vinyl carbazole) matrix. As benzobisthiazole is a stronger electron-accepting moiety than benzobisoxazole, we anticipated that the resulting polymers would have lower lowest occupied molecular orbitals (LUMO) than their oxygen-containing analogs.

## EXPERIMENTAL

## Materials

All chemicals were purchased from commercial sources and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was dried using an Innovative Technologies solvent purification system. 9,9-Dioctylfluorene-2,7-dicarbaldehyde,<sup>15</sup> 9,9-bis(3,7-dimethyloctyl)fluorene-2,7-dicarbaldehyde,<sup>15</sup> 2,7-dibromofluorene,<sup>16</sup> 2,7-dibromo-9,9-dialkylfluorenes **2a**<sup>17</sup> and **2b**,<sup>18</sup> 2,6-dimethylbenzo[1,2-*d*;4,5-*d*']bisthiazolediethylphosphonate ester,<sup>12</sup> and 2-(2-ethoxy)ethoxyethyl bromide<sup>19</sup> were synthesized according to literature procedures. Chromatographic separations were performed using silica gel 60, using eluents as indicated.

# Instrumentation

Nuclear magnetic resonance spectra were obtained on a 400 MHz spectrometer (<sup>1</sup>H at 400 MHz and <sup>13</sup>C at 100 MHz). <sup>1</sup>H NMR samples were referenced internally to residual protonated solvent. <sup>13</sup>C NMR spectra were referenced to the middle carbon peak of CDCl<sub>3</sub>. In both instances, chemical shifts are given in  $\delta$  relative to solvent. High-resolution mass spectra were recorded on a double focusing magnetic sector mass spectrometer using EI at 70 eV. Melting points were obtained using a melting point apparatus, upper temperature limit 260 °C. Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPC Max 280 separation module equipped with three 5  $\mu$ m I-gel columns connected in a series (guard, HMW, MMW, and LMW) with a refractive index detector. Analyses were performed at 35 °C using THF as the eluent with the flow rate at 1.0 mL/min. Calibration was based on polystyrene standards. Fluorescence spectroscopy and UV-visible spectroscopy were obtained using polymer solutions in chloroform and as thin films. The films were made by spin-coating  $25 \times 25 \times 1 \text{ mm}^3$  glass slides, using a solution of 10 mg of polymer per 1 mL chloroform at a spin rate of 2000 rpm. Thermal gravimetric analysis measurements were made within the temperature interval of 25-850 °C, with a heating rate of 20 °C/min, under ambient atmosphere. Differential scanning calorimetry (DSC) was performed with a first scan at a heating rate of 15 °C/min to erase thermal history and a second scan to measure transitions from 0 to 200 °C under nitrogen. Electrochemical properties were measured on an eDaq e-corder 410 potentiostat using a three-electrode cell (electrolyte: 0.1 mol/L TBAPF<sub>6</sub> in acetonitrile) with an Ag/AgNO<sub>3</sub> reference electrode, a platinum auxiliary electrode, and a platinum button electrode as the working electrode. Polymer films were drop-cast from a chloroform solution on to the working electrode. All films were annealed at 160 °C for 1 h prior to use. All cyclic voltammetry experiments were performed under argon atmosphere and were recorded at a scan rate of 100 mV/s and referenced to ferrocene/ferrocenium. Powder diffraction patterns of thin films were obtained using a Riguku Ultima IV X-Ray diffractometer equipped with an MPA-U4 multipurpose Eulerian cradle and 1.76 kW Cu K $\!\alpha$ radiation. Samples were first scanned from 0.05 to 0.501°  $2\theta$ using parallel-beam optics to determine the critical angle of the films.<sup>20</sup> The incident angles of the X-ray beam for the diffraction studies were chosen to be at a value slightly above the external critical reflection for the polymer films. Fluorescence lifetime measurements were performed using the timecorrelated-single-photon counting method. Pulses tunable from  $\sim$ 780 to 880 nm were produced from a homebuilt 82-MHz mode-locked Ti:sapphire oscillator pumped by a 5 -W Nd:VO<sub>4</sub> laser (Millennia, Spectra Physics). The resulting fundamental wavelength at  $\sim$ 814 nm was modulated by a Pockels cell (Model 350-160, Conoptics) to reduce the repetition rate to  $\sim$ 8.8 MHz. The frequency-doubling of this laser source by a harmonic generator (Model TP-2000B, U-Oplaz Technologies) provided the excitation wavelength at  $\sim$ 407 nm. A half-wave plate and polarizer placed before the sample chamber ensured vertically polarized excitation. Emission (2500 nm) was collected in a perpendicular geometry and passed through a polarizer set at the magic angle (54.7°) for solutions and 90° for solid films, with respect to the excitation polarization. For polymer solution lifetime measurements, dilute solutions of each were prepared in chloroform and placed in a 1 cm path-length cuvette. Notably, a front-faced geometry was also used for solid films. The placement of appropriate filters before the microchannel plate, MCP (Hamamatsu, R3809U-50) eliminated the excitation light and allowed selection of emission from the sample. The full width at half-maximum of the instrument response function was  $\sim$ 37-40 ps. All measurements were made in a 3-5 ns time window with a total of 4096 channels. A total of 65,536 counts were collected at the peak channel for all lifetime measurements. The fluorescence quantum yield measurements were conducted by using an Ar<sup>+</sup> laser as excitation source and a homemade integrating sphere connected to a calibrated Ocean Optics spectrometer through an optical fiber, as described elsewhere.<sup>21</sup>

## **Monomer Synthesis**

## 2,7-Dibromo-9,9-bis(2-(2-ethoxy)ethoxyethyl)fluorene

A round-bottom flask was charged with 2,7-dibromofluorene (27.05 g, 83.5 mmol) and potassium iodide (1.39 g, 8.35



mmol) in dimethyl sulfoxide (70 mL). The mixture was cooled in a cold-water bath and stirred as potassium hydroxide power (23.45 g, 418 mmol) was added in a single portion. 2-(2-Ethoxy)ethoxyethyl bromide (36.0 g, 184 mmol) was added dropwise while keeping the pot temperature between 0 and 20 °C. The reaction was stirred at room temperature for 24 h and then poured into water. The mixture was extracted with chloroform (3  $\times$  125 mL) and the organic extracts were combined, washed with brine, dried over MgSO<sub>4</sub>, and the solvent evaporated. The excess alkyl bromide was removed by distillation under reduced pressure and the remaining residue was purified by column chromatography using silica gel and a 5:1 mixture of chloroform: ethyl acetate as the eluent to yield a white solid (28.80 g, 62% yield).

 $\begin{array}{l} Mp = 88\text{--}89 \ ^\circ\text{C}; \ ^1\text{H} \ \text{NMR} \ (\text{CDCl}_3) \ \delta: \ 7.53 \ (\text{s}, \ 2\text{H}), \ 7.51 \ (\text{d}, \ 2\text{H}), \ 7.46 \ (\text{d}, \ 2\text{H}), \ 3.42 \ (\text{q}, \ 4\text{H}), \ 3.33 \ (\text{t}, \ 4\text{H}), \ 3.20 \ (\text{t}, \ 4\text{H}), \ 2.78 \ (\text{t}, \ 4\text{H}), \ 2.35 \ (\text{t}, \ 4\text{H}), \ 1.15 \ (\text{t}, \ 6 \ \text{H}); \ ^{13}\text{C} \ \text{NMR} \ (\text{CDCl}_3) \ \delta: \ 151.0, \ 138.5, \ 130.8, \ 126.8, \ 121.8, \ 121.3, \ 70.3, \ 69.8, \ 66.9, \ 66.8, \ 52.0, \ 39.6, \ \text{and} \ 15.2; \ \text{HRMS} \ (\text{EI}) \ \text{Calcd. for} \ C_{25}\text{H}_{33}\text{Br}_2\text{O}_4 \ (\text{MH}^+) \ 555.0740, \ \text{found} \ 555.0744, \ \text{and} \ \text{deviation} \ -0.7 \ \text{pm}. \end{array}$ 

# 2,7-Bis(hydroxymethyl)-9,9-bis(2-(2-ethoxy) ethoxyethyl)fluorene

A flame-dried three-neck round-bottom flask was placed under argon and charged with 2,7-dibromo-9,9-bis(2-(2ethoxy)ethoxyethyl)fluorene (15.75 g, 28.3 mmol) and dry THF (270 mL). The mixture was cooled to -78 °C and stirred as tert-butyllithium (1.7 M in pentane, 100 mL) was added dropwise via an addition funnel. It was then stirred an additional 1 h at -78 °C before adding paraformaldehyde (2.55 g, 85 mmol) in small portions over 15 min. The reaction was then stirred for another 2 h after which it was warmed to room temperature and stirred overnight. The reaction was then quenched by the addition of a saturated aqueous ammonium chloride solution and the mixture was extracted with diethyl ether (3  $\times$  100 mL). The organic extracts were combined, washed with water and brine, and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude oil was purified by column chromatography on a silica gel column using a gradient of 10:1-2:1 of diethyl ether: isopropyl alcohol to yield a yellow oil (8.22 g, 63% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 7.63 (d, 2H), 7.42 (s, 2H), 7.32 (d, 2H), 4.72 (s, 4H), 3.39 (q, 4H), 3.30 (t, 4H), 3.15 (t, 4H), 2.75 (t, 4H), 2.38 (t, 4H), 2.32 (s, 2H), 1.12 (t, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 149.5, 140.3, 139.7, 126.3, 122.0, 119.8, 69.8, 69.7, 67.1, 66.5, 65.5, 51.2, 39.6, and 15.0; HRMS (EI) Calcd. for C<sub>27</sub>H<sub>38</sub>O<sub>6</sub>Na (MNa<sup>+</sup>) 481.2561, found 481.2558, deviation 0.57 ppm.

# 9,9-Bis(2-(2-ethoxy)ethoxyethyl)fluorene-2,7dicarboxaldehyde (2 c)

A round-bottom flask was charged with 2,7-bis(hydroxymethyl)-9,9-bis(2-(2-ethoxy)ethoxyethyl)fluorene (4.62 g, 10.1 mmol) and activated manganese dioxide (6.96 g, 80 mmol) in benzene (70 mL). A Dean-Stark trap with a condenser was attached to the flask and the reaction was refluxed overnight. The mixture was then cooled to room temperature and passed through a short silica gel plug using benzene as the eluent. The solvent was evaporated yielding a yellow oil (4.56 g, 99% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 10.08 (s, 2H), 7.99 (s, 2H), 7.92 (m, 4H), 3.35 (q, 4), 3.24 (t, 4H), 3.12 (t, 4H), 2.78 (t, 4H), 2.49 (t, 4H), 1.09 (t, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 192.1, 151.6, 145.1, 136.7, 130.3, 124.7, 121.6, 70.3, 69.8, 67.1, 66.8, 52.1, 39.5, and 15.3; HRMS (EI) Calcd. for C<sub>27</sub>H<sub>35</sub>O<sub>6</sub> (MH<sup>+</sup>) 455.2428, found 455.2434, deviation -1.29 ppm.

# **General Procedure for Polymerization**

A flame-dried Schlenk flask was placed under an argon atmosphere and charged with compounds **1** (1 mmol) and **2(a-c)** (1 mmol) followed by addition of THF (30 mL). The mixture was stirred while potassium *tert*-butoxide (1.0 M in THF, 2.2 mL) was added dropwise over 20 min. The reaction was then stirred for 24 h followed by precipitation of the polymer in methanol (~100 mL). The solid was filtered and washed in a Soxhlet extractor with methanol, followed by hexanes, and then extracted with THF. The THF fraction was evaporated to yield the solid polymer.

# Poly[(9,9-dioctylfluorene-2,7-vinylene)-alt-benzo [1,2-d;4,5-d']bisthiazole-2,6-diyl] (P1)

The polymer was obtained as an orange solid (510 mg, 81% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 8.44 (s, Ar—H), 7.38–7.86 (br m, Ar—H and vinylic =C—H), 2.05 (s, —CH<sub>2</sub>—), 1.02–1.28 (br m, —CH<sub>2</sub>—), 0.59–0.92 (br m, —CH<sub>2</sub>— and CH<sub>3</sub>); GPC:  $M_{\rm n}$  = 11,500,  $M_{\rm w}$  = 32,900, and PDI = 2.9.

# Poly[(9,9-bis(3,7-dimethyloctyl)fluorene-2,7-vinylene)alt-benzo[1,2-d;4,5-d']bisthiazole-2,6-diyl] (P2)

The polymer was obtained as an orange solid (427 mg, 62% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 8.37 (s, Ar—H), 7.38–7.74 (br m, Ar—H and vinylic =C—H), 1.98 (br m, -CH<sub>2</sub>—), 0.38–1.40 (br m, -CH<sub>2</sub>— and -CH<sub>3</sub>); GPC:  $M_{\rm n}$  = 13,000,  $M_{\rm w}$  = 38,000, and PDI = 2.9.

# Poly[(9,9-bis(2-(2-ethoxy)ethoxyethyl))fluorene-2,7-vinylene)-alt-benzo[1,2-d;4,5-d']bisthiazole-2,6-diyl] (P3)

The polymer was obtained as an orange solid (386 mg, 60% yield).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 8.47 (s, Ar—H), 7.41–7.82 (br m, Ar—H and vinylic =C—H), 3.16–3.45 (br m, -0—CH<sub>2</sub>—), 2.92 (br s, -0—CH<sub>2</sub>—), 2.49 (br s, -0—CH<sub>2</sub>—), 1.27 (s,  $-CH_2$ —), 0.89 (s,  $-CH_3$ ); GPC:  $M_n = 7$  349,  $M_w = 15,300$ , PDI = 2.1.

**PLED Fabrication and Characterization.** PLEDs were fabricated on nominally 20  $\Omega$ /sq, 140-nm thick ITO-coated glass substrates (Colorado Conecpt Coatings). The substrates were first cleaned with a detergent and organic solvents and then treated in a UV/ozone oven to increase the work function of the ITO and hence facilitate hole injection, as described elsewhere.<sup>22</sup> A 60 nm PEDOT:PSS layer was spin-coated onto the ITO and then baked in air at 120 °C for 1 h, then in an argon filled glovebox at 120 °C for another 30 min. Blends of PVK and benzobisthiazole copolymers in chlorobenzene solutions were spin-coated on top of the PEDOT:PSS layer in the argon



SCHEME 1 Synthesis of poly(fluorene vinylene-alt-benzobisthiazole)s.

filled glovebox. The combined concentration of the PVK and guest material was kept constant at 9 mg mL<sup>-1</sup>. The solution was spin-coated at 4000 rpm for 60 seconds. The fabricated structure was then annealed at 60 °C for 30 min. Following this annealing step, the samples were transfered to a thermal evaporator within the glovebox and the Bphen, LiF, and Al layers were deposited sequentially by thermal evaporation at a base pressure of ~1 × 10<sup>-6</sup> Torr. The PLEDs were characterized by monitoring their EL spectra, brightness as a function of the applied voltage, and luminous and power efficiencies.

## **RESULTS AND DISCUSSION**

# Synthesis and Characterization

9,9-Bis(2-(2-ethoxy)ethoxyethylfluorene-2,7-dicarboxaldehyde 2c was synthesized in three steps starting from 2,7-dibromofluorene using methods analogous to those for the synthesis of 2a and 2b. All fluorene monomers were carefully purified via column chromatography to remove any monoalkylated side products that could lead to defects in the polymer.<sup>23</sup> The base-catalyzed Horner-Wadsworth-Emmons (HWE) polycondensation reaction between the benzobisthiazole monomer 1 and fluorene monomers 2a, 2b, and 2c in anhydrous THF afforded the polymers P1, P2, and P3 respectively (Scheme 1). The HWE reaction is preferable because it is known to produce polymers with all trans-double bonds while preventing cross-linking, incomplete double bond formation, and other undesirable structural defects.<sup>24</sup> All polymers were obtained in 60-81% yields after purification by Soxhlet extraction with methanol to remove residual salts, followed by hexanes to remove the lower molecular weight material, and finally THF to recover the soluble polymer. The THF was evaporated to yield solid polymer. All of the polymers were soluble in common organic solvents, such as mcresol, chloroform, o-dichlorobenzene, and THF. The <sup>1</sup>H NMR spectra for polymers P1, P2, and P3 were in agreement with the proposed polymer structures (see Supporting Information Figs. S10-S12). The number-average molecular weights  $(M_{\rm n} {\rm s})$  of these polymers as determined by GPC against polystyrene standards in THF range from 7500 to 13,700 g/mol with polydispersity indices [PDIs, PDI = weight-average molecular weight  $(M_w)/M_n$  of 2.1–2.9, as shown in Table 1. Based on these results number-averaged degree of polymerizations between 11 and 18 were calculated. The thermal stability of the benzobisthiazole polymers were evaluated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA curves are shown in Figure 1 and the data is summarized in Table 1. All of the polymers were found to be thermally stable with weight loss onsets occurring above 250 °C. As expected, the introduction of flexible side chains onto the polymer backbone results in significantly lower decomposition temperatures in comparison to related poly(phenylenevinylene benzobisthiazole), which does not possess side chains and exhibits 5% weight loss at 560 °C.<sup>10(a)</sup> However, the decomposition temperatures of these polymers are all high enough to be useful in semiconducting applications. Additionally, DSC indicated that none of the polymers had glass transition temperatures, which is desirable for good color purity in PLEDs.<sup>25</sup>

#### **Optical and Electrochemical Properties**

The UV-vis absorption and PL spectra of the polymers, both as dilute solutions in chloroform and as thin solid films, were evaluated. The normalized absorption and PL spectra for all of the polymers in solution is shown in Figure 2, the film spectra are shown in Figure 3, and the data is summarized in Table 2. It is apparent that the alkyl chains have no impact on the optical properties of the polymers as the absorption spectra for all of the polymers are virtually identical and possess two absorption bands, due to vibronic coupling. In comparison to the solution spectra, in the thin film spectra there is a broadening of the absorption band and the intensities of the transitions have switched. As a result the higher energy peak is now more intense than the lower energy peak. There is also a slight red-shift in the absorption of the polymers (6-11 nm), due to conformational changes in going from solution phase to solid and/or pi-stacking. In either case this effect is small for all of the polymers, an indication that the side chains do not affect the solid-state packing. This is supported by X-ray analysis, which shows that thin films of all polymers are completely amorphous with no observable periodicity (see Supporting Information Fig. S2). The optical band gap  $(E_{g}^{opt})$  was determined from

**TABLE 1** Physical Properties of Poly(fluorene vinylene-altbenzobisthiazole)s

Polymer	<i>M</i> <sub>n</sub> <sup>a</sup>	<i>M</i> <sub>w</sub> <sup>a</sup>	PDI	<i>T</i> <sub>d</sub> <sup>b</sup> (°C)
P1	11,500	32,900	2.9	361
P2	13,000	38,200	2.9	258
P3	7,350	15,280	2.1	276

<sup>a</sup> Determined by GPC in THF using polystyrene standards.

<sup>b</sup> 5% weight loss temperature by TGA.





**FIGURE 1** TGA plot of poly(fluorene vinylene-*alt*-benzobisthiazole)s.

the absorption onset of the polymer films and was 2.4 eV for all of the polymers, further evidence that alkyl chain substitution has no effect on the electronic properties of these materials.

The PL of the polymers in solution shows a narrow bluegreen emission at  $\sim$ 490 nm which is independent of alkyl chain substitution as the emission spectra are essentially the same for all of them. All of the polymers show a significant red-shift in their film PL spectra into the orange region of the visible spectrum relative to their emissions in solution which indicates that the polymer chains adopt a more planar conformation in solid state.<sup>26</sup> The wavelength of emitted light is similar for all of the polymer films (558–560 nm) and is also independent of alkyl chain substitution. **P3** exhibits a broader emission band than **P1** and **P2** a result of increased aggregation in the **P3** film relative to **P1** and **P2**. This is due to the inability of the 2-(2-ethoxy)ethoxyethyl chains of **P3** to effectively disrupting  $\pi$ -stacking compared to the alkyl chains on **P1** and **P2**. This is evident from the reduced solubility and molecular weight of **P3**.

The redox properties of the polymers were evaluated using cyclic voltammetry (see Supporting Information Fig. S13 for voltammograms). The calculated electron affinities (EA) and IPs are listed in Table 2. All of the polymers had partially reversible reduction waves with reduction onsets at -1.9, -1.8, and -1.8 V for P1, P2, and P3 respectively. These reduction potentials translate to EAs of 2.9, 3.0, and 3.0 eV which are larger than the homopolymer poly(9,9-dihexylfluorene-2,7-vinylene), which has an EA of 2.7 eV,<sup>27</sup> a consequence of incorporating the benzobisthiazole moiety into the conjugated backbone. The EAs for these new polymers are within range of previously reported poly(arylene vinylene-co-fluorene)s with electron withdrawing moieties in the backbone (2.83-3.17 eV).<sup>7(c),28</sup> This indicates that the electron-deficient benzobisthiazole moiety is beneficial for increasing the EA of conjugated polymers. The polymers did not show oxidative reversibility but gave onsets of 0.7, 0.8, and 0.7 V for P1, P2, and P3, which corresponds to IPs of 5.5, 5.6, and 5.5 eV, respectively. Both the EAs and IPs of these polymers are the structurally higher than analogous poly[(9,9-



FIGURE 2 UV-vis absorption (solid lines) and PL (dashed lines) of P1, P2, and P3 in chloroform solutions.



FIGURE 3 UV-vis (solid lines) and fluorescence (dashed lines) of thin films of P1, P2, and P3.

## **TABLE 2** Electronic and Optical Properties of Benzobisthiazole Polymers

	Solution		Thin Film					
Polymer	$\lambda^{max}$ (nm)	λ <sub>em</sub> (nm)	$\lambda_{max}$ (nm)	λ <sub>em</sub> (nm)	$E_{g}^{opt}$ (eV) <sup>a</sup>	$E_{g}^{EC}$ (eV)	EA (eV) <sup>b</sup>	IP (eV) <sup>c</sup>
P1	451, 480 <sup>d</sup>	492 <sup>d</sup> , 527	486, 455 <sup>d</sup>	559	2.4	2.6	2.9	5.5
P2	449, 478 <sup>d</sup>	491 <sup>d</sup> , 526	485, 454 <sup>d</sup>	558	2.4	2.6	3.0	5.6
P3	446, <sup>d</sup> 475	488 <sup>d</sup> , 522	486, 456 <sup>d</sup>	560	2.4	2.5	3.0	5.5

<sup>a</sup> Optical band gap measured from the onset of absorption in films.

 $^{\rm b}$  Electron affinity calculated from reduction onset ( ${\it E}_{\rm red})$  in CV trace using EA  $=-({\it E}_{\rm red}+4.8).$ 

 $^{\rm c}$  lonization potential calculated from oxidation onsent (  $E_{\rm ox})$  in CV trace using IP  $=-(E_{\rm ox}$  + 4.8).

<sup>d</sup> Denotes highest intensity peak.

dioctylfluorene-2,7-vinylene)-*alt*-benzo[1,2-*d*;4,5-*d'*]bisoxazole-2,6-diyl] (PFVBBO) (EA = 2.87 eV, IP = 5.36 eV) which has oxygen atoms in place of sulfur in the backbone.<sup>15</sup> The electron density is more equally shared between sulfur and carbon in benzobisthiazole than between oxygen and carbon in benzobisoxazoles, since sulfur is less electronegative than the oxygen atom. Therefore, the  $\pi$ -orbitals will be more delocalized, making benzobisthiazole a better electron-accepting moiety. Additionally the empty d-orbitals of the sulfur atom can contribute to the molecular  $\pi$ -orbitals decreasing the energy of the  $\pi$ - $\pi$ \* transition.<sup>8(b),29</sup> Collectively this causes benzobisthiazole polymers to have lower EAs. The higher IPs are a consequence of the increased aromaticity of the thiazole ring over the oxazole, which stabilizes the HOMOs of **P1-3**.<sup>11(b)</sup> The resulting electrochemical band gaps are in close agreement with the optical band gaps and these results are further evidence that the alkyl chain substitution has no impact on the electronic properties of these polymers.

The PL decay lifetimes of the polymers were measured both in dilute solutions and thin films and the results summarized in Table 3. In solution, the polymers show relatively short lifetimes of 0.46–0.60 ns but are comparable to the previously mentioned PFVBBO polymer which had a PL decay lifetime of 0.51 ns.<sup>15</sup> In films, the lifetimes for PL decay were even shorter (0.07–0.15 ns) due to solid-state interchain interactions leading to various non-radiative decay pathways, thus quenching film fluorescence. **P3** showed a much larger drop off in decay lifetimes than **P1** and **P2**, which can be attributed to the greater extent of aggregation in the **P3** film. The decay rate for **P1** in film is identical to that of the structurally analogous PFVBBO (also 0.12 ns), which suggests replacing the oxygen atoms in PFVBBO with sulfur atoms does not affect PL decay.

PL quantum yields were measured for all three polymers and it was found that in solution all of the polymers were efficient fluorophores with yields between 0.54 and 0.62. In solution, the alkyl chain substitution did not have a significant impact on quantum yield and all three polymers had yields similar to that of PFVBBO ( $\Phi = 0.68$ ). In thin films, as seen with the PL decay lifetimes, the quantum yield fell to near zero. This is an effect of concentration quenching of the polymers in film and has also been reported for PFVBBO.

## **Electroluminescent Devices**

We first examined the use of the polymers as neat emitting layers in PLEDs with the structure ITO/PEDOT:PSS (60 nm)/ P1-P3/BPhen (40 nm)/LiF (1 nm)/Al (100 nm), where ITO is indium tin oxide, PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate), and BPhen is 4,7-diphenyl-1,10-phenanthroline. However, due to low solid-state quantum yields, electroluminescence was not observed. Because of their high quantum yield in solution, these polymers are good candidates for guest-host PLEDs. We therefore fabricated PLEDs where the polymers were used as low level dopants in poly(N-vinylcarbazole) (PVK) matrix. The device architecture was ITO/PEDOT:PSS (60 nm)/PVK:P1-P3/ BPhen (40 nm)/LiF (1 nm)/Al (100 nm), and the PVK had an average molecular weight 50,000-100,000 g/mol). The devices were optimized by varying the weight percentage (wt %) of P1, P2, or P3 in PVK and the properties of the resulting devices are shown in Table 4. As the concentration of guest polymer in PVK was increased, overall performance decreased with the most efficient devices made from 1 wt %polymer guest in PVK. Concentration quenching was particularly evident in the devices containing P3, which did not show significant emission from the guest at any concentration. The device containing 1 wt % of P2 in PVK exhibited the best efficiency at 0.61 Cd/A with a brightness of 478  $Cd/m^2$ . This efficiency is higher than the 0.25 Cd/A obtained from a similar device containing PFVBBO.<sup>15</sup> The improved efficiency over PFVBBO can be attributed to the higher EA of P2, which may improve the electron injection and transport,

**TABLE 3** Photoluminescence Decay Lifetimes ( $\tau$ ) and Quantum Yields ( $\Phi$ )

	Solut	ion <sup>a</sup>	Thin Film		
Polymer	τ (ns) <sup>b</sup>	Φ	$\tau$ (ns) <sup>b</sup>	Φ	
P1	0.47	0.54	0.12	< 0.01	
P2	0.46	0.62	0.15	< 0.01	
P3	0.60	0.56	0.07	<0.01	

<sup>a</sup> Taken in dilute chloroform solutions.

<sup>b</sup> Photoluminescence decay lifetimes were obtained using a triexponential decay fit.



<b>TABLE 4</b> Device Characteristic	of PLEDs Made From	Benzobisthiazole Poly	ymers
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Device <sup>a</sup>								
Polymer	wt %	V <sub>on</sub> <sup>b</sup> [V]	Drive Voltage [V]	Current Density [J, mA/cm <sup>2</sup> ]	Brightness [Cd/m <sup>2</sup> ]	Efficiency [Cd/A, %EQE <sup>c</sup> ]	$\lambda_{max}^{}^{}$ [nm]	CIE 1931 [ <i>x</i> , <i>y</i> ]
PVK	0.0	5.8	11.2	306	250	0.31, 0.30	423	(0.17, 0.07)
P1	1.0	7.3	10.8	753	478	0.30, 0.25	499, 428	(0.18, 0.15)
	2.0	8.3	13.0	770	289	0.24, 0.17	499, 425	(0.19, 0.20)
	4.0	9.4	17.6	543	195	0.14, 0.08	499, 427	(0.20, 0.25)
P2	1.0	7.4	11.2	392	478	0.61, 0.45	502, 429	(0.19, 0.18)
	2.0	8.7	13.4	377	452	0.35, 0.20	504, 428	(0.22, 0.27)
	4.0	7.8	12.8	377	323	0.21, 0.12	505, 429	(0.24, 0.31)
P3	1.0	6.6	9.8	358	199	0.25, 0.35	-, <b>429</b>	(0.17, 0.08)
	2.0	6.4	10.2	240	208	0.22, 0.29	-, 429	(0.17, 0.09)
	4.0	7.0	10.8	311	213	0.19, 0.22	495, 427	(0.17, 0.11)

<sup>a</sup> Device structure: ITO/PEDOT:PSS/PVK:(**P1**, **P2**, or **P3**)/BPhen/LiF/AI. wt % is weight percent of polymer in PVK.

<sup>b</sup> Turn-on voltage (at which EL is visible to the eyes).

<sup>c</sup> EQE = external quantum efficiency.

leading to a higher population of electron charge carriers in the device.

Still, the overall efficiencies of these devices are low and the electroluminescence spectra of the polymers (Fig. 4) suggest a possible reason for this. In all of the devices, PVK emission at ~425 nm dominates the spectrum, overshadowing the guest emission at ~500 nm, which implies inefficient Förster resonance energy transfer between the host and guest. The degree of energy transfer depends on the overlap of the host's emission spectrum with the guest's absorption band.<sup>30</sup> Because these polymers have absorptions much more redshifted (~480 nm) than PVK emission (~425 nm), there is poor spectral overlap between the two. This results in a decrease in guest emission and a reduction in overall device performance. These materials could benefit from using a host with a narrower band gap that would give better spectral overlap, improving the energy transfer.

## CONCLUSION

In summary, three new solution-processible benzobisthiazolefluorene-containing polymers were synthesized via HWE condensation polymerization. Changing the alkyl chains on the fluorene units did not lead to a change in the electronic properties of the materials but did improve the solubility of the polymers in organic solvents while maintaining high thermal stabilities. The optical and electrochemical properties of the polymers showed that incorporation of the benzobisthiazole moiety increased their EAs relative to fluorene homopolymers. Preliminary electroluminescent devices made from these polymers showed promising brightness with modest efficiencies. These results demonstrate that the benzobisthiazoles are not as good as benzobisoxazoles for the development of electrondeficient emissive materials for PLEDs. However, these materials may find use as electron-transporting materials, this work is currently ongoing and will be reported in due course.



FIGURE 4 Electroluminescent spectra of the benzobisthiazole polymers in guest-host PLEDs.

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