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Synthesis and Characterization of Poly(5,8-quinoxaline ethynylene)s

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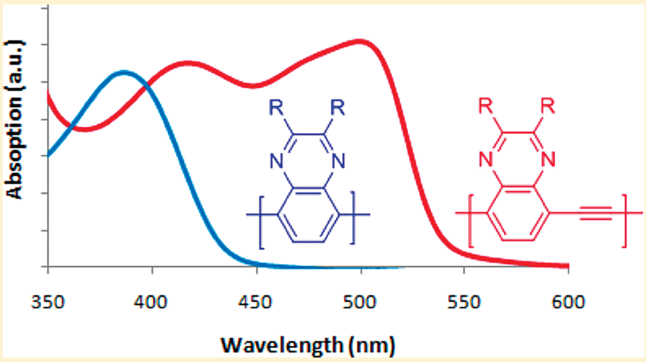
S *Supporting Information*

ABSTRACT: A majority of conjugated organic polymers are electron-rich materials, with far fewer electron-poor (i.e., electron accepting) analogues. Here we report the synthesis and preliminary characterization of new class of electron-poor poly(arylene ethynylene)s (PAEs) that contain 5,8-quinoxaline ethynylene repeat units. While various PAE copolymers consisting of alternating electron-rich and electron-poor units display lower bandgaps than poly(phenylene ethynylene)s, the poly(5,8-quinoxaline ethynylene) (PQE) reported in this study has a higher electron affinity and lower bandgap (2.25 eV) than many of these donor−acceptor materials. In comparison to poly(5,8-quinoxaline)s (PQs), which do not have an ethynylene linkage between the quinoxalines, the PQE has a red-shifted absorption spectrum that is consistent with a more highly conjugated and planar backbone. In addition, the PQE has a lower electrochemical reduction potential than both a corresponding PQ and a donor−acceptor alternating PAE copolymer that contains the quinoxaline unit as the electron-poor component.



INTRODUCTION

Research initiatives in the design and synthesis of novel conjugated polymers for use in organic electronics have resulted in the preparation of a multitude of materials that possess a wide array of properties.[1] However, most of these are electron-rich polymers with low oxidation potentials. These display p-channel semiconduction and may serve as electron donors in heterojunction devices. The electron-accepting materials in such devices are typically small molecules that have a high electron affinity, such as [6,6]-phenyl-C_{61}-butyric acid methyl ester, PCBM.[2] Employing an electron-poor polymer as the electron-accepting material in heterojunction devices could provide advantages over the use of small molecules, such as better control of phase separation and less costly material processing. However, there are far fewer reports of electron-poor conjugated polymers (i.e., those with high electron affinity) than there are of electron-rich materials. One example of the use of a cyano-substituted poly(phenylene vinylene) as the electron acceptor in a bulk-heterojuction solar cell reports power conversion efficiencies of ca. 2%, suggesting that other electron-poor polymers may have a role in the development of heterojunction devices.[3]

Electron accepting conjugated polymers generally contain electron withdrawing substituents such as fluorine[4] or cyano groups,[5] or have nitrogen-containing heteroaromatic units in the conjugated backbone (e.g., quinoline,[6] pyramidine,[7] pyridine,[8] thienopyrazine,[9] and quinoxaline[10,11]). For example, poly(5,8-quinoxaline), PQ, has a relatively high electron afffinity ($E_{red} = -2.00$ V versus Ag/Ag^+), and the backbone of the polymer is easily decorated with flexible side chains to afford soluble analogues.[12] Several quinoxaline-containing donor−acceptor alternating copolymers have been explored in efforts to prepare low band gap and electroluminescent materials, including those with thiophene,[13−15] fluorene,[16−18] and phenylene[19] units.

One common criteria for the preparation of low band gap conjugated polymers is the need for a structure in which the conjugated backbone can adopt a planar conformation. This increases the effective conjugation length and promotes close packing of the polymer chains, and thereby enhances intermolecular electronic interactions.[20] The direct connection between the quinoxaline units of poly(5,8-quinoxaline) imparts repulsive steric interactions between neighboring repeat units, Figure 1. This leads to twisting around the arene−arene bond which impedes planarization and close packing of the conjugated backbone. In contrast, poly(arylene ethynylene)s (PAEs), in which an ethynylene unit is inserted between the aromatic units, often adopt a planar structure that facilitates crystalline packing of the chains in the solid state.[21] The rigid structure, strong fluorescence, and solid state packing of PAEs have led to their use in a variety of applications including sensors[22] and liquid crystal displays.[23] Thus, we set out to explore the synthesis and electronic properties of poly(5,8-quinoxaline ethynylene), PQE, which consists of electron-poor quinoxaline units separated by ethynylene linkages. This is unusual among the PAEs in that the arylene units are exclusively electron-poor heteroarenes. The properties

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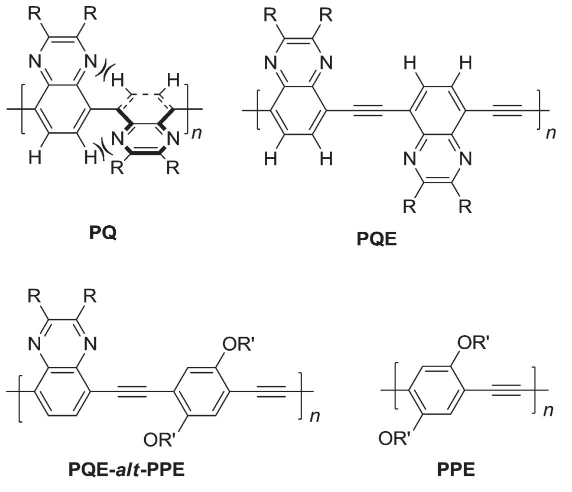

Figure 1. Poly(5,8-quinoxaline ethynylene), PQE, and PQ, PPE, and PQE-*alt*-PPE analogues. The direct connection of quinoxalines in PQ imparts repulsive interactions between neighboring repeat units.

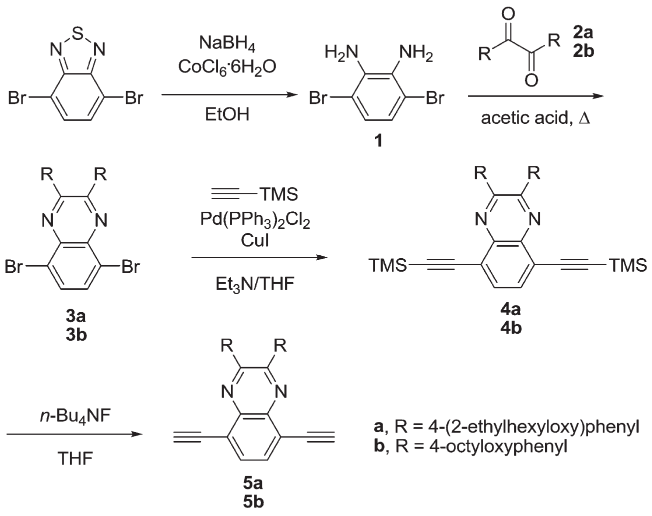

Figure 2. Synthesis of dibromoquinoxaline (3) and diethynyl quinoxaline (5) monomers.

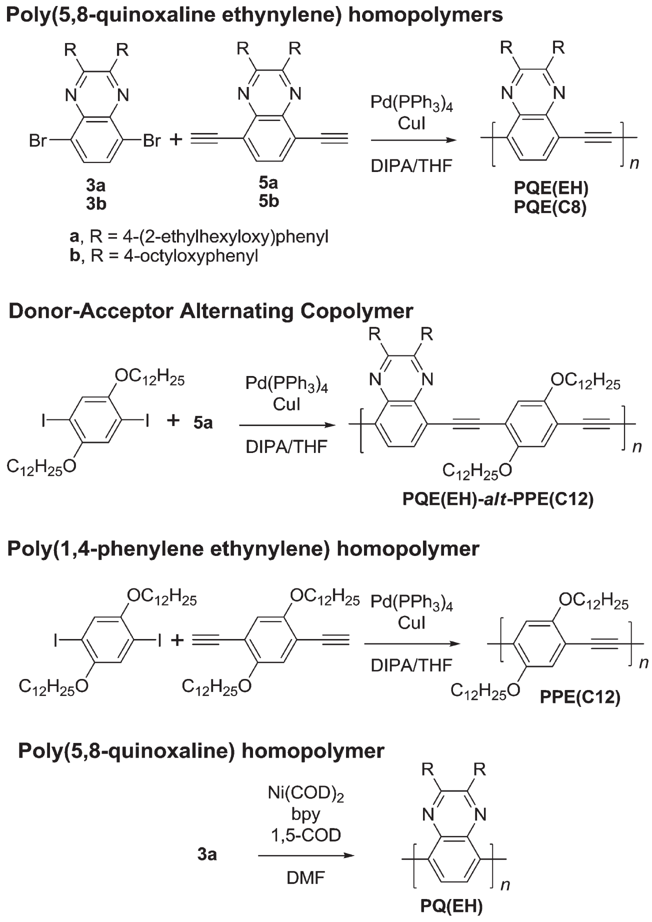

Figure 3. Synthesis of quinoxaline polymers, donor—acceptor alternating copolymer, PPE and PQ.

of these polymers are compared to those of an electron-rich PAE, poly(1,4-phenylene ethynylene) (PPE);[24,25] a poly(5,8-quinoxaline) (PQ);[12] and a polymer consisting of alternating quinoxaline ethynylene units and 2,5-dialkoxy-1,4-phenylene ethynylene units (PQE-*alt*-PPE), Figure 1.[26] The latter is one example of a class of donor—acceptor alternating PAE copolymers consisting of an electron-rich 2,5-dialkoxy-1,4-phenylene ethynylene unit and an electron-poor heteroarene ethynylene (e.g., benzotriazole ethynylene,[27] quinoline ethynylene,[28] and quinoxaline ethynylene[26]). The alternating donor—acceptor motif of this class of polymers has been explored extensively as an approach to prepare conjugated polymers with lower band gaps than PAEs that contain a single type of arene unit.

The poly(5,8-quinoxaline ethynylene)s in this study were prepared by palladium-catalyzed cross-coupling of a 2,3-disubstituted 5,8-dibromoquinoxaline, **3**, and the similarly substituted 5,8-diethynylquinoxaline, **5**, Figure 2. Both monomers were substituted with either 4-(2-ethylhexyloxy)phenyl (analogues **a**) or 4-octyloxyphenyl side chains (analogues **b**) in the 2- and 3-positions of the quinoxaline ring to impart solubility. The 5,8-dibromoquinoxalines were prepared according to published procedures with minor modifications, Figure 2.[29] Dibromobenzothiadiazole was reduced with sodium borohydride to afford diamine **1**. In an optimized procedure **1** was used without purification in a subsequent condensation with α-dione **2a** or **2b** to give the 5,8-dibromoquinoxaline monomers **3a** and **3b**, respectively. Sonogashira coupling of trimethylsilylacetylene and the 5,8-dibromoquinoxalines afforded the corresponding TMS-protected 5,8-diethynylquinoxalines, **4**. Subsequent desilylation upon treatment with tetra-*n*-butylammonium fluoride afforded the 5,8-diethynylquinoxaline monomers, **5**.

Palladium-catalyzed coupling of 5,8-dibromoquinoxalines **3** and 5,8-diethynylquinoxalines **5** afforded the correponding poly(5,8-quinoxaline ethynylene)s, Figure 3. The polymers were precipitated from the reaction mixture by addition to a large volume of MeOH, and the precipitate was purified by successive extractions with acetone, hexanes and chloroform in a Soxhlet extractor. The acetone and hexanes extractions removed catalyst and low molecular weight oligomers. The PQE bearing 4-(2-ethylhexyloxy)phenyl side chains, **PQE(EH)**, was extracted into chloroform. This afforded a material with M_n = 19 kg/mol and PDI = 2.1. The remaining polymer in the Soxhlet thimble was insoluble in common organic solvents. The chloroform fraction of **PQE(EH)** was characterized by ^{1}H NMR and IR spectroscopy (see Supporting Information for spectra). Unlike

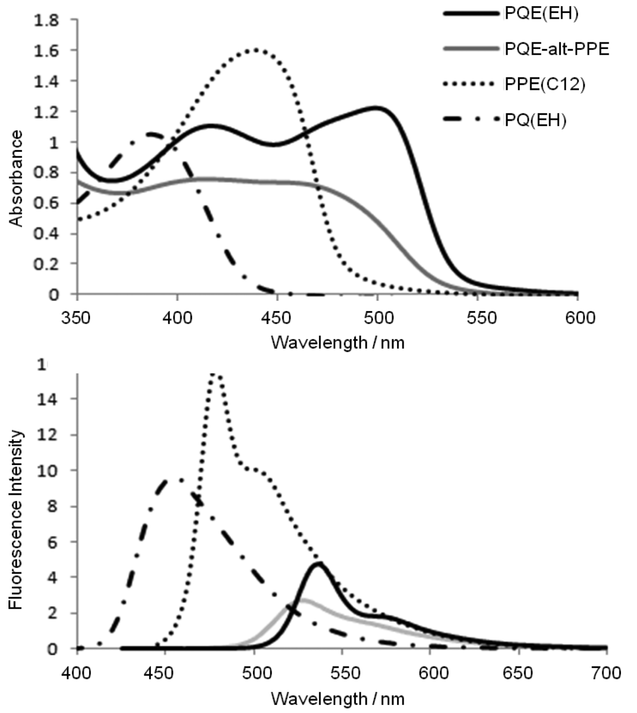

Figure 4. UV−vis absorption spectra (top) and fluorescence spectra (bottom) of solutions of polymers: **PQE(EH)** (black line), **PQ(EH)** (dashed line), **PQE(EH)-*alt*-PPE(C12)** (gray line) and **PPE(C12)** (dotted line). Solutions in chloroform at a concentration of 50 μg/mL.

poly(5,8-quinoxaline vinylenes), which undergo degradation in a matter of minutes in light and air,[10] the poly(quinoxaline ethynylene)s in this study are stable in light and air (observed over a number of weeks). The PQE with 4-octyloxyphenyl side chains, **PQE(C8)**, was insoluble in common organic solvents and was not further characterized.

The donor−acceptor alternating copolymer **PQE(EH)-*alt*-PPE(C12)** was synthesized by Sonogashira coupling of diethynyl quinoxaline monomer **5a** and 1,4-bis(dodecyloxy)-2,5-diiodobenzene, Figure 3.[26] After extraction with acetone and hexanes to remove catalyst and unreacted monomers the remaining red solid was only partially soluble in hot organic solvents such as chloroform and 1,1,2,2-tetrachloroethane. The ^{1}H NMR spectra of the material soluble in $CDCl_3$ and 1,1,2,2-dichloroetane were consistent with the polymeric structure. Poly(2,5-didodecyloxy-1,4-phenylene ethynylene), **PPE(C12)**, was synthesized by polymerization of the 2,4-di(dodecyloxy)-substituted 1,4-diiodo- and 1,4-diethynylbenzene monomers by Sonogashira coupling.[25] The polyquinoxaline poly(2,3-(4-(2-ethylhexyl)oxyphenyl)quinoxaline-5,8-diyl), **PQ(EH)**, was prepared by Yamamoto cross-coupling polymerization of 5,8-dibromoquinoxaline, **3a**, Figure 3.[12]

The absorption spectra of solutions of **PPE(C12)** and **PQ(EH)**, and the quinoxaline-based PAEs (**PQE(EH)** and **PQE(EH)-*alt*-PPE(C12)**) were obtained in chloroform at a concentration of 50 μg/mL, Figure 4. Poly(5,8-quinoxaline) **PQ(EH)** has an absorption maximum at 390 nm, which is consistent with the previously reported value for this polymer.[12] The corresponding PAE analogue, poly(5,8-quinoxaline ethynylene), **PQE(EH)**, has a significantly broader and red-shifted absorption with two maxima, at 422 and 505 nm. The large red-shift of the maxima and absorption edge (550 nm) of **PQE(EH)** compared to **PQ(EH)** is consistent with the greater conjugation of the former, resulting from a more planar structure arising from separation of the quinoxaline units by the ethynylene linkages. The absorption of **PQE(EH)** is also significantly red-shifted compared to that of **PPE(C12)**, which has an absorption maxima at 447 nm. The absorption spectrum of the alternating quinoxaline−dialkoxyphenylene PAE, **PQE(EH)-*alt*-PPE(C12)**, is also very broad, and slightly blue-shifted relative to **PQE(EH)**.

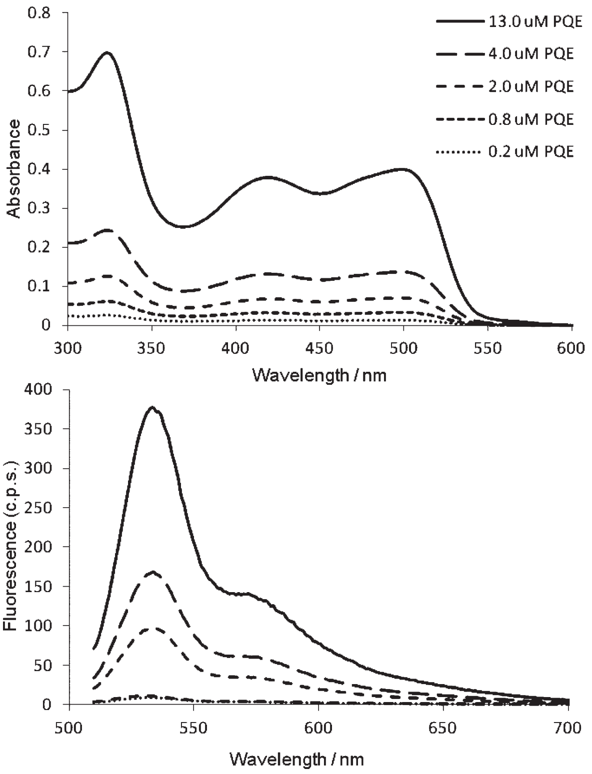

Figure 5. Absorption and emission spectra of PQE(EH) at various concentrations in $CHCl_3$. Top, ultraviolet−visible absorption spectra; Bottom, emission spectra.

The fluorescence spectra of the polymers were also obtained, Figure 4. In solution, poly(quinoxaline ethynylene) **PQE(EH)** has an emission at 531 nm, which is red-shifted with respect to the corresponding polyquinoxaline **PQ(EH)** (451 nm). As with the absorption spectra, this shift is consistent with a more planar structure arising from separation of the quinoxaline units by the ethynylene units. Both of the quinoxaline-based PAEs in this study, **PQE(EH)** and the alternating donor−acceptor polymer **PQE(EH)-*alt*-PPE(C12)**, have much lower fluorescence intensity than either the dialkoxy PPE, **PPE(C12)**, and the poly(5,8-quinoxaline), **PQ(EH)**. To explore whether the lower fluorescence intensity and the appearance of two peaks in the absorption spectra of **PQE(EH)** might arise from aggregation in solution,[30] we collected spectra over a wide range of concentrations, Figure 5. The similarity of the spectra over this range of concentrations leads us to believe that these features do not arise from aggregation in solution with separate contributions from the aggregated and nonaggregated forms.

The absorption spectra of films of the polymers were obtained by spin-casting solutions of the polymers in chloroform (20 mg/mL) onto quartz slides, Figure 6. The absorption maxima of the polymers and the optical band gaps are given in Table 1 (see Supporting Information for spectra). All of the conjugated polymers in this study have red-shifted absorption maxima compared to the solution spectra as a result of the close contact and electronic interactions between the polymer chains in the solid state. Films of poly(5,8-quinoxaline ethynylene) **PQE(EH)** gave two maxima, at 406 and 516 nm. In common with the spectra of solutions of the polymers, these are significantly red-shifted with respect to the absorption maxima of the corresponding polyquinoxaline, **PQ(EH)**. We note that the solid-state absorption of **PQE(EH)** has little to no red shift compared to the solution state spectra, although we have discounted the likelihood that the long wavelength absorption in the latter arises from aggregation. The optical bandgap of **PQE(EH)** determined from the absorption onset is 2.25 eV, which is significantly less than that of **PQ(EH)** (2.73 eV). Films suitable for determining the solid state spectra of **PQE(EH)-*alt*-PPE(C12)** could not be prepared due to the low solubility of the polymer. However, a previously reported alternating quinoxaline ethynylene-phenylene copolymer bearing different side chains has a bandgap of 2.30 eV.[31] Thus, while the incorporation of alternating electron-deficient and electron-rich arenes into the backbone of PAEs remains an attractive approach to prepare low band gaps materials,[31] the PQE reported here has a slightly lower bandgap than the donor-acceptor materials reported to date, Table 1.

To further explore the potential for poly(quinoxaline ethynylene)s to serve as an electron-accepting material we collected emission spectra of solutions of poly(3-hexylthiophene), **P3HT**, containing various concentrations of **PQE(EH)**, Figure 7. While **P3HT** displays a strong emission with a maximum at 508 nm, the intensity of this peak is diminished by increasing concentrations of **PQE(EH)**, indicating facile charge transfer between the two materials.

Cyclic voltammograms of the polymers were collected by drop casting chloroform solutions of the polymers (15 mg/mL) onto an Au working electrode. Polyquinoxaline **PQ(EH)** exhibits a reduction peak at −2.10 V versus a Ag/AgCl quasi-reference electrode, and a reoxidation potential at −1.72 V, Figure 8, which is consistent with previously reported values for similarly substituted polyquinoxalines.[12] The poly(5,8-quinoxaline ethynylene) **PQE(EH)** displays a lower oxidation potential displaying a reduction wave with at−1.27 V and a reoxidation peak at −1.19 V. The redox behavior remains the same upon repeated cycling of the potential. No oxidation peaks are observed in excursions to positive potentials (up to +1 V) for either polymer. The poly(5,8-quinoxaline ethynylene)s also have lower reduction potential than the alternating PAE copolymer consisting of 3,8-quinoxaline and 2,4-dialkoxy-1,4-phenylene units, **PQE-*alt*-PPE** (−1.54 V).[26] Accordingly, **PQE(EH)** has a greater electron affinity than related PAE materials. In comparison, PCBM, a benchmark for electron-accepting materials in organic electronics, has a reduction potential of ca. −0.6 V versus Ag/AgCl.[32]

In conclusion, we have described the preparation of a new class of electron-accepting polymers, poly(5,8-quinoxaline ethynylene)s, consisting of alternating quinoxaline and ethynylene segments in the polymer backbone. This is the first example of the broad class of poly(arylene ethynylene)s consisting entirely of electron-accepting heteroaromatic repeat units. These materials have good stability in light and air and are much more

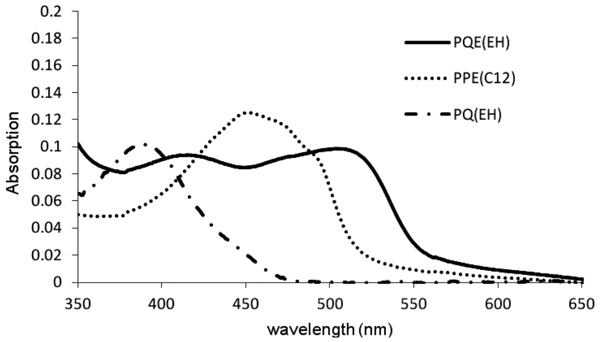

Figure 6. Solid-state UV−vis absorption spectra of poly(5,8-quinoxaline ethynylene) **PQE(EH)** (solid line), poly(5,8-quinoxaline) **PQ(EH)** (dashed line), and poly(1,4-phenylene ethynylene) **PPE(C12)** (dotted line).

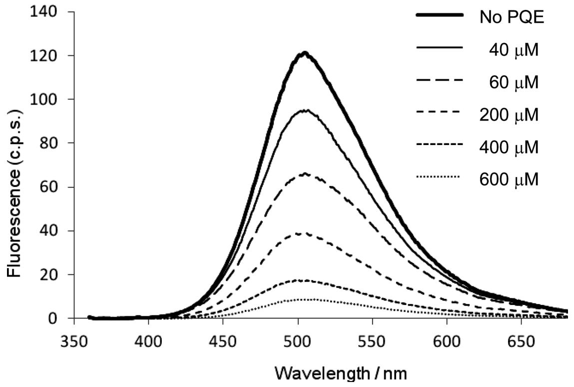

Figure 7. Fluorescence spectra from 30 μM solutions of **P3HT** in $CHCl_3$ in the presence of **PQE(EH)**. Concentrations refer to the molar concentration of repeat units of the two polymers in solution.

Table 1. Optical Properties of the Quinoxaline-Based and Dialkoxy PPE Polymers and Copolymers

	solution ($CHCl_3$)		thin films		
	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	E_g^{opt} (eV)
PQE(EH)	422, 505	531	406, 516	554	2.25
PQ(EH)	390	451	395	498	2.73
PPE(C12)	447	477	467	563	2.38
PQE(EH)-*alt*-PPE(C12)	410−470	521	-[a]	-[a]	-[a]
PQE(Ph)-*alt*-PPE(EtHex)[b]	462	538	493	558	2.30
phenylene-*alt*-benzotriazole PAE[c]	445	500	463	560	2.36
phenylene-*alt*-quinoline PAE[d]	430	560	412	605	2.30

[a] Data could not be obtained due to low solubility. [b] Alternating copolymer containing poly(phenylene ethynylene-*alt*-quinoxaline ethynylene), see ref 26. [c] Poly(phenylene ethynylene-*alt*-benzotriazole ethynylene); see ref 27. [d] Poly(phenylene ethynylene-*alt*-quinonline ethynylene); see ref 28.

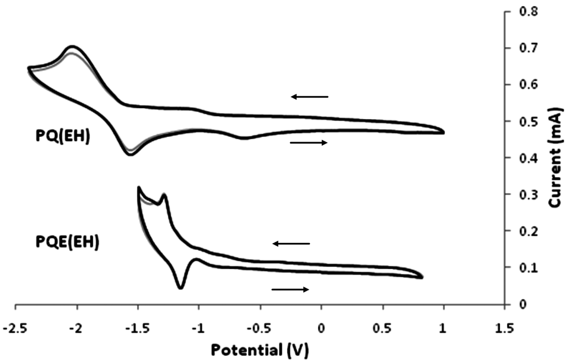

Figure 8. Cyclic voltammograms of films of poly(5,8-quinoxaline) **PQ(EH)** (top) and poly(5,8-quinoxaline ethynylene) **PQE(EH)** (bottom) on Au immersed in a 0.1 M solution of tetrabutylammonium perchlorate in acetonitrile (100 mV/s sweep rate, potentials reported against a Ag wire quasi-reference electrode) . The black curve represents the first potential cycle; the gray represents the second.

soluble than the alternating donor−acceptor copolymer, **PQE-*alt*-PPE**. In comparison to polyquinoxalines, the poly(5,8-quinoxaline ethynylene)s have red-shifted optical absorptions. This corresponds to a lower band gap resulting from the planarization of the backbone upon incorporation of the ethynylene linkages to relieve steric interactions between the quinoxaline rings that are present in PQ. In addition to a lower bandgap, the PQEs have a higher electron affinity than corresponding polyquinoxalines and donor−acceptor copolymers. Accordingly, these materials may be useful as an electron-accepting material for a variety of applications. Matching the absorption spectra of dissimilar conjugated materials to the solar spectrum, and matching the energy levels and band gaps of conjugated materials are key to the development of heterojunction devices.[33] The exploration of PAEs that incorporate electron poor heteroarenes, as well as copolymers, offers new opportunities to further tailor the electronic structure and properties of conjugated polymers to serve as electron accepting-materials.

■ EXPERIMENTAL SECTION

All starting materials were purchased from commercial sources and used without further purification. THF and Et_2O were dried over sodium benzophenone ketyl prior to distillation under argon. Column chromatography was performed on flash grade silica (32−60 Å, Sorbent Technologies, Atlanta, Georgia). Thin-layer chromatography was performed on 3 × 5 cm silica gel plates (0.2 mm thick, 60 F254) on an aluminum support (Sorbent Technologies). NMR analysis was performed on a Bruker DSX 400 or DSX 300 instruments using $CDCl_3$ as the solvent. Chemical shifts are reported relative to internal tetramethylsilane. IR analyses were performed on a Nicolet 4700 FTIR with an ATR attachment from SmartOrbit Thermoelectronic Corporation. GPC analyses were performed on a Waters 2690 Separations Module with a Waters 2410 refractive index detector at a flow rate of 1 mL/min, determined by gel permeation chromatography, relative to polystyrene standards. Ultraviolet−visible analysis was performed on a Perkin-Elmer Lambda 19 spectrophotometer, and fluorescence spectroscopy was performed on a Shimadzu RF-5301PC spectrofluorophotometer. Cyclic voltammetry experiments were performed on a BAS100B electrochemical analyzer, where thin films were cast onto an Au working electrode in a 0.1 M solution of tetrabutylammonium perchlorate in acetonitrile using a Pt auxiliary electrode and a silver wire quasi reference electrode at a scan rate of 100 mV/s. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, Georgia). 4,7- Dibromobenzo[c][1,2,5]-thia-diazole,[34] 1,4-bis(dodecyloxy)-2,5-diethynylbenzene and 1,4-bis-(dodecyloxy)-2,5-diiodobenzene[25,35] were prepared by previously reported procedures. Synthetic prodecures and characterization of homologues **a** (*R* = 4-(2-ethylhexyloxy)phenyl) are provided below. Homologues **b** (*R* = 4-octyloxyphenyl) were synthesized using similar procedures unless otherwise stated. Procedures and spectral characterization of homologue **b** and polymers **PQE(EH)-*alt*-PPE(C12)**, **PQ(EH)** and **PPE(C12)** is provided in the Supporting Information.

5,8-Dibromo-2,3-bis(4-(2-ethylhexyloxy)phenyl)quinoxaline, 3a. Sodium borohydride (6.7 g, 180 mmol) was added in six equal portions over 1 h to a solution of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (8.9 g, 30 mmol) and $CoCl_2\cdot 6H_2O$ (0.1 g, 0.4 mmol) in ethanol (200 mL) and stireed at room temperature for an additional 30 min. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2 (100 mL). The solution was washed with H_2O (2 × 50 mL) and dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford diamine **1** (Figure 2) that was used without further purification. The crude diamine (4.1 g, 15 mmol) was added to a solution of 1,2-bis(4-(2-ethylhexyloxy)phenyl)ethane-1,2-dione (6.9 g, 15 mmol) in acetic acid (200 mL) and the mixture was heated to reflux for 72 h under argon. The solution was poured into H_2O (800 mL) and the resulting mixture was neutralized with a 10% solution of aqueous NaOH and then extracted with CH_2Cl_2 (3 × 500 mL). The organic extracts were combined and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography (40:60 v/v CH_2Cl_2:hexanes) to afford the dibromo-quinoxaline monomer **3a** as a bright yellow viscous liquid (6.7 g, 65%): ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.84 (s, 2H, quinoxaline C−H), 7.66 (d, $^3J_{HH}$ = 9 Hz, 4H, Ph C2−H), 6.89 (d, $^3J_{HH}$ = 8.7 Hz, 4H, Ph C3−H), 3.88 (d, $^3J_{HH}$ = 6 Hz, 4H, $-OCHH_2-$), 1.70−1.76 (m, 2H), 1.26−1.52 (m, 16H), 0.86−0.98 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.69 (Ph C4), 153.57 (quinoxaline C2 and C3), 132.43 (quinoxaline C6 and C7), 131.60 (Ph C2), 130.24 (Ph C1), 123.40 (quinoxaline C5 and C8), 114.39 (Ph C3), 70.55 (C−O), 39.29, 30.47, 29.06, 23.81, 23.03, 14.08, 11.09. IR (ATIR): 2916 (Ar C−H str.), 1244, 1169 (C−O str), 1603 (C=N str.), 1478, 1379 (C−C str.), 538 (C−Br str.) 1510, 1331, 1288, 1009, 984, 899, 829, 731, 654, 611 cm^{-1}. HRMS: calcd for $C_{36}H_{44}N_2O_2Br_2$ = 694.1770; obsd = 694.1746; Δ = 3.5 ppm. Anal. Calcd: C, 62.07; H, 6.37; N, 4.02. Found: C, 62.16; H, 6.40; N, 4.04.

2,3-Bis(4-(2-Ethylhexyloxy)phenyl)-5,8-bis((trimethylsilyl)-ethynyl)quinoxaline, 4a. A mixture of dibromoquinoxaline **3a** (6.6 g, 9.5 mmol) in THF (20 mL) and triethylamine (10 mL) was degassed by two freeze−pump−thaw cycles. $Pd(PPh_3)_2Cl_2$ (0.64 g, 0.91 mmol) and CuI (0.27 g, 1.4 mmol) were added to the solution, followed by tetramethylsilyl acetylene (1.9 g, 20 mmol), and the mixture was stirred at 50 °C for 24 h. H_2O (1 mL) was added and the solvent was removed under reduced pressure. The resulting residue was taken up in CH_2Cl_2 (80 mL) and the solution was washed with H_2O (150 mL). The solvent from the organic extracts was removed under reduced pressure and the resulting residue was purified by column chromatography (30:70 v/v CH_2Cl_2: hexanes) to afford the TMS-protected monomer **4a** as a yellow solid (4.7 g, 67%): mp = 118.6−119 °C. ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.75 (s, 2H, quinoxaline C−H), 7.70 (d, $^3J_{HH}$ = 8.7 Hz, 4H, Ph C2−H), 6.86 (d, $^3J_{HH}$ = 8.7 Hz, 4H, Ph C3−H), 3.87 (d, $^3J_{HH}$ = 5.7 Hz, 4H, $-OCHH_2-$), 1.68−1.75 (m, 2H), 1.28−1.52 (m, 16H), 0.88- 0.96 (m, 12H), 0.35 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.52 (Ph C4), 152.36 (quinoxaline C2 and C3), 140.67 (quinoxaline C1 and C4), 132.54 (quinoxaline C6 and C7), 131.56 (Ph C2), 131.00 (Ph C1), 123.04 (quinoxaline C5 and C8), 114.16 (Ph C3), 103.18 ($C\equiv C-TMS$), 101.48 ($C\equiv C-TMS$), 70.58 (C−O), 39.45, 30.50, 29.09, 23.83, 23.04, 14.1, 11.12. IR (ATIR): 2918 (Ar C−H str.), 2148 ($C\equiv C$ str.), 1244, 1176 (C−O str.), 1600 (C=N str.), 1478, 1379 (C−C str.), 542

(C−Br str.) 1512, 1460, 1063, 1014, 831, 756, 627 cm^{-1}. HRMS: calcd for $C_{46}H_{62}N_2O_2Si_2$ = 730.4350; obsd = 730.4360; Δ = 1.4 ppm. Anal. Calcd: C, 75.56; H, 8.55; N, 3.83. Found: C, 75.55; H, 8.45; N, 3.87.

2,3-Bis(4-(2-ethylhexyloxy)phenyl)-5,8-diethynylquinoxaline, 5a. A solution of tetra-*n*-butylammonium fluoride (1 M in THF, 6 mL, 6 mmol) was added to a solution of **4a** (2.0 g, 2.7 mmol) in THF (16 mL) under argon. The mixture was stirred at room temperature for 45 min and H_2O (50 mL) was added. The mixture was extracted with CH_2Cl_2 (2 × 30 mL), the organic extracts were combined and the solvent was removed under reduced pressure. The residue was purified by column chromatography (40:70 v/v CH_2Cl_2: hexanes) to afford the diethynyl−quinoxaline monomer **5a** as an orange viscous liquid (1.18 g, 73%). ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.83 (s, 2H, quinoxaline C−H), 7.62 (d, $^3J_{HH}$ = 8.7 Hz, 4H, Ph C2−H), 6.87 (d, $^3J_{HH}$ = 9 Hz, 4H, Ph C3−H), 3.87 (d, $^3J_{HH}$ = 6 Hz, 4H, −OCHH$_2$−), 3.61 (s, 2H), 1.70−1.78 (m, 2H), 1.26−1.55 (m, 16H), 0.88−0.98 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.51 (Ph C4), 153.33 (quinoxaline C2 and C3), 140.96 (quinoxaline C1 and C4), 133.20 (quinoxaline C6 and C7), 131.57 (Ph C2), 130.91 (Ph C1), 122.71 (quinoxaline C5 and C8), 114.36 (Ph C3), 85.00 ($C{\equiv}C$−H), 80.18 ($C{\equiv}C$−H), 70.56 (C−O), 39.29, 30.48, 29.06, 23.81, 23.04, 14.09, 11.1. HRMS calcd for $C_{40}H_{46}N_2O_2$ = 586.3559; obsd = 586.3565; Δ = 1.0 ppm. IR (ATIR): 3236 ($C{\equiv}C$−H str.) 2918 (Ar C−H str.), 2148 ($C{\equiv}C$ str.), 1244, 1176 (C−O str.), 1600 ($C{=}N$ str.), 1478, 1379 (C−C str.), 542 (C−Br str.) 1512, 1460, 1063, 1014, 831, 756, 627 cm^{-1}. Anal. Calcd: C, 81.87; H, 7.90; N, 4.77. Found: C, 82.01; H, 7.88; N, 4.84.

Poly(5,8-(2,3-bis(4(2-ethylhexyloxy)phenyl)quinoxaline ethynylene), PQE(EH). A solution of dibromoquinoxaline **3a** (1.0 g, 1.8 mmol) and diethynylquinoxaline **5a** (3.7 g, 5.3 mmol) in THF (25 mL) was degassed by two freeze−pump−thaw cycles. Diisopropylamine (5.0 mL, 35 mmol), CuI (55 mg, 0.29 mmol), and $Pd(PPh_3)_4$ (0.40 g, 0.35 mmol) were added, and the mixture was and heated at 45 °C for 24 h. The mixture was poured into methanol (200 mL), and the resulting precipitate was isolated by filteration. The solid was subjected to sequential extraction with acetone, hexane, and chloroform in a Soxhlet extractor. The solvent was removed from the chloroform fraction under reduced pressure to afford the quinoxaline polymer **PQE(EH)** as a red solid (0.842 g, 90%). ^{1}H NMR (300 MHz, $CHCl_3$): δ 7.78−7.67 (m, 4H), 7.40−7.37 (m, 8H), 6.80−6.7 (m, 8H), 3.94−3.68 (m, 8H), 1.26−1.55 (m, 36H), 0.95−0.84 (m, 24H). IR (ATIR): 2954 (Ar C−H str.), 1255, 1165 (C−O str), 1371 (C−C str.), 2848, 1599, 1509, 1254, 1003, 999, 787, 685, 498 cm^{-1}. GPC (THF, refractive index detector): M_n = 19 kg/mol, PDI = 2.1. Anal. Calcd: C, 75.73; H, 7.46, N, 4.71. Found: C, 75.19; H, 7.24; N, 4.05.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures for analogues **b** and polymers used to compare spectroscopic data (**PQE(EH)-*alt*-PPE(C12)**, **PPE(C12)**, and **PQ((EH))**, and solid state spectra. This material is available free of charge via the Internet at http://pubs.acs.org/.

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