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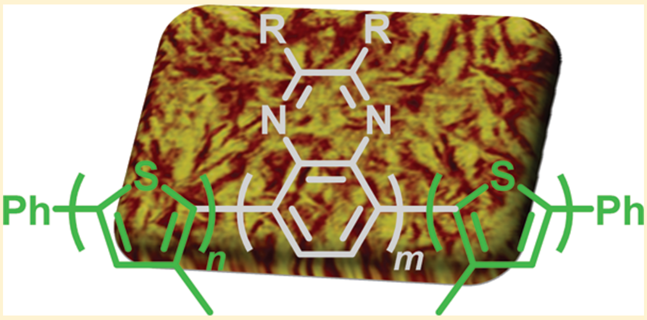
Synthesis and Characterization of Fully Conjugated Donor–Acceptor–Donor Triblock Copolymers

Kathy B. Woody,[†] Benjamin J. Leever,[‡] Michael F. Durstock,[‡] and David M. Collard[†,*]

[†]School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States
[‡]Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, United States

S *Supporting Information*



ABSTRACT: A synthetic approach is established to provide a monofunctional telechelic poly(3-octylthiophene) (**P3OT**) bearing a single bromine-substituted end group that is of potential use in the preparation of well-defined block copolymers. Telechelic **P3OT** was prepared via a chain growth process by a catalyst-transfer condensation polymerization (CTCP) of 5-bromo-4-octyl-2-thienylmagnesium iodide initiated by a phenylnickel(II) initiator. Optimization of the conditions for quenching the reaction allowed for the installation an α-bromo functionality at the terminus of the polymer. We demonstrate the utility of this well-defined monofunctional polymer, **Ph–P3OT–Br**, by coupling it to a poly(quinoxaline) (**PQ**) bearing boronate ester end groups to provided a new class of donor–acceptor–donor (D–A–D) triblock copolymers. The formation of the triblock copolymers was confirmed by gel-permeation chromatography (GPC) and ^{1}H NMR spectroscopy. The optical properties of the polymers were investigated using UV–visible absorption and fluorescence spectroscopy. Efficient quenching of the fluorescence from the individual blocks of the triblock copolymers is consistent with the occurrence of electron transfer. AFM images illustrate a nanoscale phase separation of the electron-rich **P3OT** and electron-poor **PQ** blocks.

INTRODUCTION

Conjugated polymers have been widely studied for use as organic semiconductors in electronic devices such as solar cells. These materials have the potential to provide low-cost, flexible, and lightweight devices for which the cost of materials processing is significantly lower than for inorganic semiconductors.[1] In bulk-heterojuction (BHJ) organic solar cells, donor (D) and acceptor (A) materials are blended to provide the photoactive layer. Absorption of photons leads to the formation of excitons, and diffusion of these excitons to the D–A interface leads to formation of charge carriers.[2] For example, prototype photovoltaic cells incorporating a regioregular poly(3-alkylthiophene) as the donor and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) as the acceptor display promising efficiencies.[3] Initiatives to improve the performance of organic solar cells largely focus on the design and synthesis of new low band gap conjugated polymers[4] and changing the morphology of the blends.[5] Thoroughly blending of the donor and acceptor materials improves device performance by reducing the size of the phase-separated domains such that they are on the order of the exciton diffusion length (10–20 nm).[6]

Block copolymers phase separate on the nanoscale and the size of the phases formed by the two blocks is directly related to the length of each block. Rod–coil block copolymers containing a semirigid conjugated segment and a flexible segment have been extensively studied and provide abundant opportunities to prepare materials with unique morphologies, however these polymers only contain one electroactive segment.[7–11] Donor–acceptor block copolymers with a conjugated electron donating segment and an aliphatic segment containing pendant electron acceptors have also been prepared.[12–14] However, the aliphatic segment in rod–coil block copolymers serves as an insulator. There are few examples of fully conjugated block copolymers, which either have an aliphatic spacer between the conjugated segments[3,15] or are directly linked.[16] The paucity of fully conjugated D–A block copolymers can largely be attributed to the synthetic challenges in preparing such materials and the lack of electron accepting polymers, which generally contain nitrogen-based heteroaromatic units in the conjugated backbone (e.g., pyridine,[17] quinoxaline,[18] quinoline,[19] or thienopyrazine[20]) or are substituted with electron-withdrawing substituents (e.g., fluorine[21] or cyano substituents[22]). Such block copolymers could provide opportunities to control the scale and morphology of phases in BHJ devices.

The development of new synthetic methodologies is required to provide access to donor–acceptor block polymers that make use of the phase separation of the two blocks to impart new or

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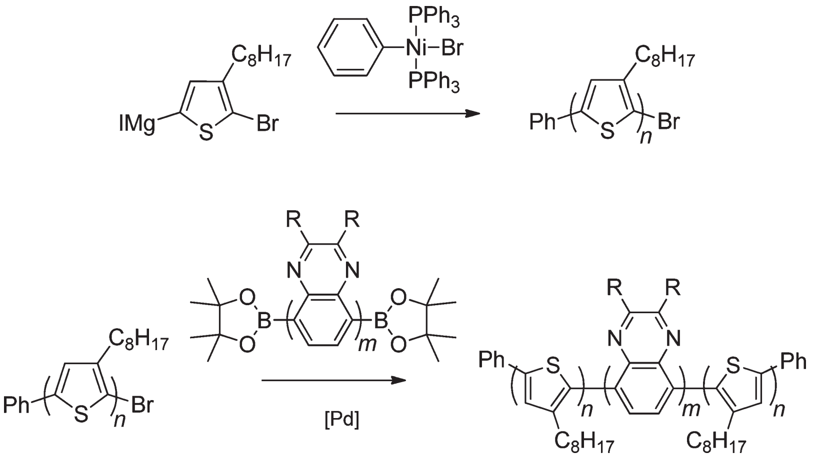

Figure 1. Preparation of a telechelic poly(3-octylthiophene) with a single α-bromothienyl end group, and coupling to a poly(5,8-quinoxaline) (PQ) bearing two boronate ester end groups to afford a triblock copolymer.

enhanced electronic properties. One approach used to prepare donor−donor (D−D) fully conjugated block copolymers is to couple the termini of two separate prepolymers that bear complementary functionality.[16,23,24] More recently, with the advent of catalyst-transfer condensation polymerizations (CTCP) of haloarylmagnesium halides,[25] similar D−D block copolymers architectures have become accessible by chain extension of the active end of quasi-living polymers with a second monomer.[26−31] Here we describe the use of CTCP to prepare a telechelic poly(3-octylthiophene) (P3OT) bearing a single bromine-substituted end group that is of potential use in the preparation of well-defined block copolymers. We demonstrate the utility of this new well-defined monofunctional polythiophene by coupling it under Suzuki coupling conditions to a poly(quinoxaline) (PQ) that has two boronate ester end groups. This provides a D−A−D triblock copolymer, Figure 1. Poly(3-alkylthiophene)s are commonly employed as a donor material in BHJ solar cells.[32] For this study, we chose poly(5,8-quinoxaline) as an electron-poor acceptor block because it is susceptible to n-doping by reduction (E_{red} = −1.98 V versus Ag/Ag$^+$) and the polymer is rendered soluble by decoration of the backbone with flexible side chains.[18] The structural and optical properties of the polymers are described.

■ RESULTS AND DISCUSSION

Synthetic Approach. Our synthetic approach to well-defined triblock copolymers involves three steps: (i) the synthesis of a well-defined monofunctional telechelic P3OT donor block that bears a single α-bromothienyl end group, (ii) the synthesis of a PQ acceptor block bearing complementary boronate ester functionality at both ends, and (iii) coupling of the two polymer chains under Suzuki cross-coupling conditions, Figure 1.

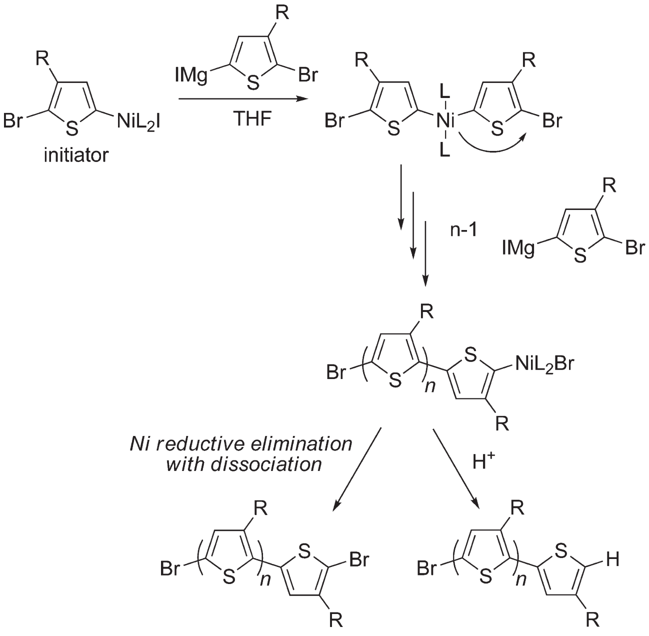

Figure 2. Origin of two types of end groups from propagating end in the catalyst-transfer condensation polymerization (CTCP) of 5-bromo-4-alkyl-2-thienylmagnesium bromides.

Telechelic Bromine-Terminated Poly(3-alkylthiophene) Donor Block. We explored several methods to attain well-defined telechelic P3OT that bears a single α-bromothienyl end group that subsequently could be coupled to a poly(5,8-quinoxaline) block. It is well established that poly(3-alkylthiophene)s with low polydispersity can be prepared by nickel(II)-catalyzed polymerization of 5-bromo-4-alkyl-2-thienylmagnesium iodides.[25] Unlike most condensation polymerizations of metalloaryl halides, this reaction proceeds by a catalyst-transfer chain growth mechanism in which the nickel remains associated with the polymer chain and the propagating end interconverts between an α-bromothienyl and an α-thienylnickel complex upon addition of each monomer, Figure 2.[33−35] The quasi-living nature of this polymerization relies on the rate of propagation being substantially greater than that of dissociative reductive elimination of nickel from the propagating chain end. While significant details about this process have been elucidated, quenching of the polymerization, typically by pouring the reaction mixture into an acidic aqueous solution, affords a mixture of α-bromothienyl (Th−Br/Th−Br) and unfunctionalized thienyl end groups (Th−Br/Th−H), Figure 2.[36] In addition, polymer chains can undergo metathesis to generate polythiophene with unfunctionalized thienyl end groups on both chain ends (Th−H/Th−H). Previously, McCullough and co-workers showed that it was possible to end-functionalize polythiophene using a Grignard reagent such as ethynylmagnesium bromine as an

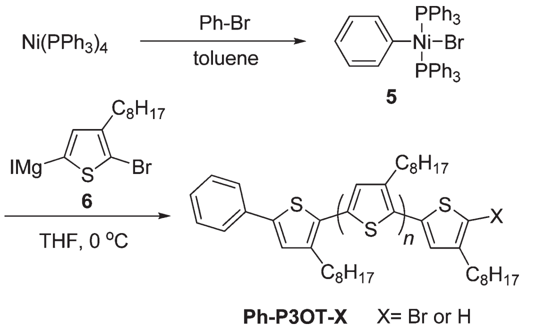

Figure 3. Initiation of the polymerization of 2-bromo-3-octyl-5-iodothiophene (**6**) with phenylnickel(II) initiator (**5**) leads to phenyl initiated P3OT.

end-capping reagent.[37] The end-functionalized polythiophene in these studies have been used to prepare rod−coil block copolymers.[8,10]

In an effort to attain further control over the preparation of poly(3-alkylthiophene), several groups have explored the use of preformed arylnickel(II) complexes as initiators, thereby resulting in the installation of the aryl group at the initiated end of the chain.[38−40] We chose to prepare poly(3-octylthiophene) by employing phenylnickel(II) bromide as an initiator, and then focus on the retention of the α-bromothienyl functionality at the terminus derived from the propagating chain end. This was guided, in part, by the proposed mechanistic origins of the different combinations of end groups.[40]

Addition of bromobenzene to a solution of Ni(PPh$_3$)$_4$ in toluene led to the precipitation of the bright yellow initiator **5** that was collected by filtration, Figure 3.[41] Initiation of the polymerization of 2-bromo-3-octyl-5-iodothiophene (**6**) with **5** at 0 °C resulted in the formation of the phenyl initiated poly(3-alkylthiophene) with either bromine or hydrogen groups at the terminus derived from the propagating chain end (i.e, **Ph−P3OT−X**) Figure 3. Kiriy has previously shown that if low temperatures are maintained during this polymerization the resulting polymers are exclusively propagated from the phenyl initiator with formation of chains with Ph/Th−Br and Ph/Th−H combinations of end groups. However, at room temperature there is evidence for chain transfer in which nickel dissociates from one chain and initiates a new chain that lacks the aryl end group derived from the initiator, resulting in chains initiated from 5-bromo-4-alkyl-2-thienylnickel(II) and end-capped with α-bromothienyl and unfunctionalized thienyl end groups (e.g., Th−Br/Th−Br and Th−Br/Th−H combinations of end-groups, plus some Th−H/Th−H as a byproduct).[40] Even in the absence of chain transfer, the α-bromothienyl end groups derived from the propagating chain end form as a result of some reductive elimination with dissociation of the nickel from the polymer backbone which could occur during the polymerization or after consumption of the monomer.

Analysis of the aromatic region of the ^{1}H NMR allows for characterization of the two termini of the phenylnickel(II)-initiated polymers, Figure 4A. The protons of the phenyl end groups derived from the initiator appear as a distinct set of multiplets at 7.61 (d), 7.38 (t), and 7.27 (m) ppm, with integrals of 2:2:1 respectively corresponding to the AM$_2$X$_2$ spin system of the phenyl end group. The β-hydrogen of the thiophene unit adjacent to the phenyl end group (H$_d$, Figure 4A) appears as a singlet at 7.16 ppm: As expected, the integral of this peak reveals a 1:1 ratio with the phenyl end groups. The thiophene at the other end of the polymer chain bears either an α-thienyl bromide or hydrogen atom (X = H or Br, Figure 4A). The relative amounts of these two types of end groups can be determined by ^{1}H NMR. The β-proton on the terminal thiophene (proton f, Figure 4) appears at 6.90 ppm if it bears an α-hydrogen atom, and at 6.83 ppm (proton f′) if the polymer is terminated with a bromine atom.[42] Initial batches of polymer prepared in this manner contained a mixture of α-bromothienyl (56%) and unfunctionalized thienyl (44%) end groups, Figure 4A. The sum of the integral of protons f and f′ (i.e., from the propagating chain end) is equal to that of the β-proton on the thiophene adjacent to the phenyl end group (proton d of the initiating end), consistent with efficient initiation of the polymerization by the phenylnicklel(II) complex **6** and chain growth without termination or chain transfer prior to quenching..

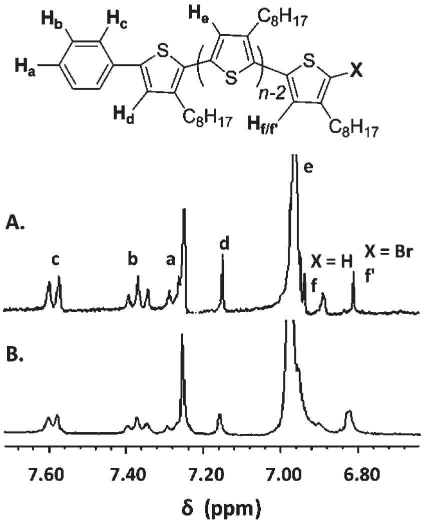

Figure 4. ^{1}H NMR (300 MHz, CDCl$_3$) of phenylnickel(II)-initiated poly(3-octylthiophene), allowed to react for 1 h and then: (A) quenched by pouring reaction mixture into MeOH; (B) maintained for 12 h at −15 °C and poured into MeOH.

This result is in contrast to a previous report in which polymerizations were conducted at room temperature. At this higher temperature a significant portion of the isolated polymers lacked the aryl end group derived from the initiator,[40] suggesting the occurrence of chain transfer whereby nickel dissociates from one propagating chain and reinitiates chain growth from another monomer. While initiation of the polymerization with the phenylnickel(II) complex installs a phenyl group at one end of the P3OT chain, the mixture of termini derived from the propagating chain end presents a significant hindrance to the preparation of block copolymers since it is important that all of the polymer chains have identical functionality. Polymers bearing an unfunctionalized thienyl end group would not undergo a subsequent coupling reaction to provide block copolymers, thereby leading to homopolymer impurities. In our hands, modifications of reaction time, temperature and quenching conditions were unsuccessful in completely preventing dissociative reductive elimination, and the polymerization reactions always gave a mixture of α-bromothienyl and thienyl termini derived from the propagating chain end. Since efforts to prevent this dissociation from occurring were unsuccessful, we decided instead to simply allow time for the dissociative reductive elimination

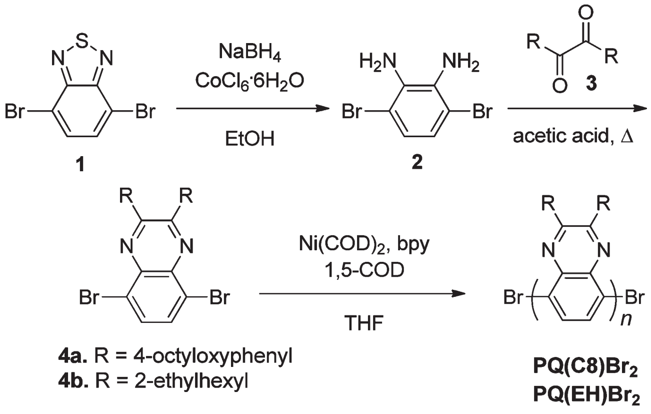

Figure 5. Synthesis of bromine terminated poly(5,8-quinoxaline) (**PQBr$_2$**).

of the nickel(II) from the polymer chain at the end of the polymerization to provide α-bromothienyl end groups. Rather than following the commonly used procedure of quenching the polymerization by pouring the reaction mixture into methanol after a relatively short reaction time (i.e., upon consumption of the monomer), the reaction mixture was placed in a freezer at −15 °C for 12 h prior to precipitation into methanol. Holding the reaction at low temperatures for an extended period after consumption of the monomer allowed for almost complete reductive elimination and dissociation of the nickel from the polymer backbone to provide P3OT terminated with α-bromothienyl end groups (**Ph−P3OT−Br**). Thus, while propagation is significantly faster than chain transfer during the polymerization, which is important to the success of this procedure, reductive elimination with dissociation of nickel from the chain does take place, albeit slowly, once the monomer is consumed. The ^{1}H NMR of the polymer reveals a 1:1 ratio of the *β*-proton on the thiophene adjacent to the phenyl propagating group (proton d, Figure 4B) and the α-bromothienyl group (proton f′, Figure 4B), consistent with a polymer containing a high proportion of phenyl groups at the initiated end and α-bromothienyl end groups derived from the propagating end (i.e., the Ph/Th−Br combination of end groups). While there is a small peak present at 6.90 ppm, the agreement in the integrals of peaks d and f′ indicate that the presence of unfunctionalized thienyl end groups is minimal. Chain transfer products which would lead to polythiophene with Th−Br/Th−Br and Th−Br/Th−H end groups are absent based on the appearance of the NMR spectra (i.e., the absence of peaks corresponding to a Th−Br initiating end, and equal integrals of peaks d and f′).

The precipitated solid was subjected to sequential extraction in a Soxhlet extractor with methanol, acetone, hexanes and chloroform. From this procedure, extracts into hexanes consisted of a material with a lower degree of polymerization (DP = 14), and the chloroform fraction provided polymer with higher molecular weight (DP = 22), and low polydispersity indices (1.2 and 1.3, respectively). In these polymerizations we employed a 1:20 initiator to monomer ratio. The molecular weights appear to be consistent with the control of the chain length by the molar ratio of the initiator and monomer, albeit the polymer has been fractionated.[25]

Boronate Ester Functionalized Poly(5,8-quinoxaline). The difunctional electron-accepting block in this study, poly(2,3-(4-octyloxyphenyl)quinoxaline-5,8-diyl), **PQ(C8)**, and poly(2,3-(2-ethylhexyl)quinoxaline-5,8-diyl), **PQ(EH)**, were prepared by condensation polymerizations of 5,8-dibromoquinoxalines **4a** and **4b** using Yamamoto coupling conditions,[18] Figure 5. Monomer **4** was synthesized by published procedures with minor modifications:[43] 4,7-Dibromobenzothiadiazole (**1**) was reduced with sodium borohydride to afford diamine **2**, which was used without purification in a subsequent condensation with diketone **3**. Nickel(0)-catalyzed polymerization of monomers **4a** and **4b** resulted in the corresponding dibromo-terminated polymers **PQ(C8)Br$_2$** and **PQ(EH)Br$_2$**, respectively. The protons of the quinoxaline rings at the termini of the chains appear as two distinct doublets in the ^{1}H NMR at 6.98 and 7.73 ppm (see Supporting Information for spectra). This is consistent with unsymmetrically substituted quinoxaline groups, and is in contrast to the signal for the symmetrically substituted quinoxaline rings in the backbone of the polymer that appear as a singlet at 8.33 ppm. The degree of polymerization of the polymer was determined by comparing the relative integrals of the protons of the end groups and those of the polymer backbone.

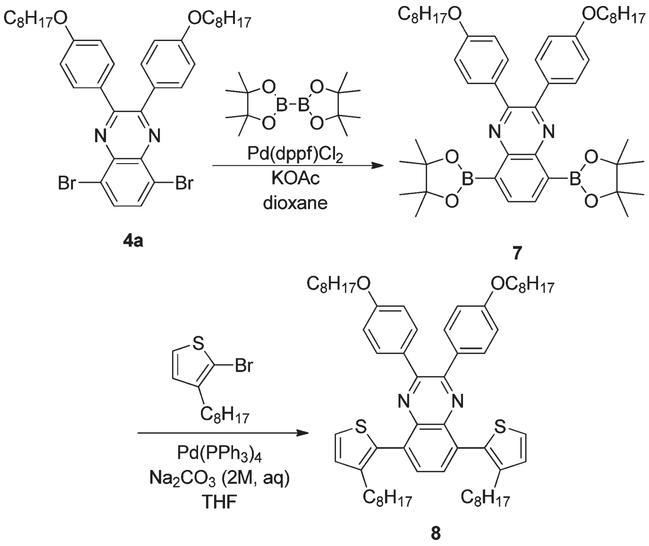

Figure 6. Synthesis of thiophene-quinoxline-thiophene trimer by Suzuki cross-coupling.

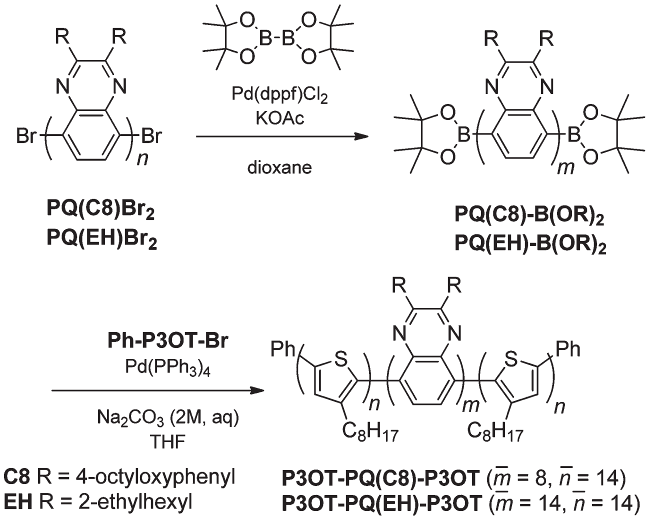

Figure 7. Synthesis of donor−acceptor−donor triblock copolymers by Suzuki cross-coupling.

The **PQ(C8)Br$_2$** sample prepared in this study had a DP of eight, and the **PQ(EH)Br$_2$** analogue had a DP of 14.

Coupling of Donor and Acceptor Blocks. We chose to convert the end groups of **PQBr$_2$** into boronate esters that could be coupled to the α-bromine terminated poly(3-octylthiophene), **Ph−P3OT−Br**, by a Suzuki cross-coupling reaction to couple the two blocks together. In order to test this approach, 5,8-dibromoquinoxaline (**4a**) was treated with an excess of bis(pinacolato)diboron. This led to rapid and quantitative conversion to bisborolane **7**, as confirmed by ^{1}H NMR (the singlet for the aromatic hydrogen of **4a** at 7.83 ppm disappeared, and a new singlet appeared at 7.93 ppm for the bisborolane-quinoxaline), Figure 6. The palladium catalyzed Suzuki cross-coupling reaction between bisborolane **7** and 2-bromo-3-octylthiophene afforded bisthienylquinoxaline **8** with an isolated yield of 92% and serves as a model for the coupling of the donor and acceptor blocks.

Treatment of **PQBr$_2$** with a large excess of bis(pinicolatediboron) afforded the boronate ester-terminated poly(quinoxaline), **PQ−B(OR′)$_2$** as a yellow powder, Figure 7. While the ^{1}H NMR signals of the aromatic end groups of the boronate ester terminated polyquinoxalines are coincident with those of the dibromo-substituted analogue, the presence of the boronate end groups was confirmed by the appearance of a C−O stretching band at 1248 cm^{-1} in the IR spectrum (see Supporting Information).

The D−A−D triblock copolymers were prepared by combining the boronate ester terminated poly(quinoxaline)s, **PQ−B(OR′)$_2$**, with 4 equiv of the hexanes-soluble **Ph−P3OT−Br** under Suzuki cross-coupling conditions, Figure 7. The lower molecular weight hexanes-soluble fraction of the poly(3-alkylthiophene) donor block was used in order to simplify the purification process after the coupling reaction whereby any unreacted polymer could be washed out of the mixture by extraction. After coupling the resulting block copolymers were precipitated by addition of the reaction mixture to a large volume of cold methanol, and the resulting solid was purified by successive extractions in a Soxhlet extractor with methanol, acetone, hexanes and chloroform. Any unreacted **Ph−P3OT−Br**, which was used in excess, was extracted into hexanes, and the block copolymer was extracted into the chloroform fraction.

Polymer Characterization. The number (M_n) and weight (M_w) average molecular weights and polydispersity (PDI) of the homopolymers and triblock copolymers were determined by GPC and ^{1}H NMR spectroscopy, Table 1. The relative segment lengths of the block copolymers were determined by integration of the ^{1}H NMR signals of the protons of the aromatic rings: The β−hydrogen atoms of the thiophene backbone of P3OT gives a singlet at 7.0 ppm and the poly(quinoxaline) gives a singlet at 8.0 ppm (see Supporting Information).

GPC profiles of **Ph−P3OT−Br**, **PQ(C8)Br$_2$** and the resulting D−A−D triblock copolymer are shown in Figure 8. The elution curve of the hexanes-soluble fraction of **Ph−P3OT−Br** (dotted line) corresponds to an M_n of 2.4 kDa. The dibromopoly(quinoxaline), **PQ(C8)Br$_2$** (dashed line), has an M_n of 5.8 kDa. After Suzuki coupling of the donor and acceptor polymers and subsequent extractions, the chloroform fraction gives an elution curve corresponding to an M_n of 10.3 kDa (solid line). Taken together the ^{1}H NMR spectra and GPC data are consistent with formation of the D−A−D triblock copolymer, **P3OT−PQ(C8)−P3OT**.

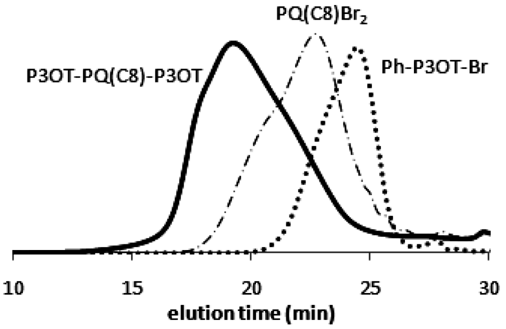

Figure 8. GPC profiles of **Ph−P3OT−Br** (dotted line), **PQ(C8)Br$_2$** (dashed line), and **P3OT-PQ(C8)−P3OT** (solid line).

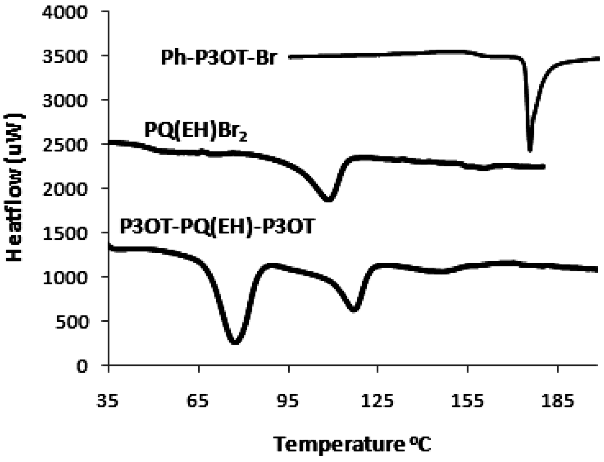

Figure 9. DSC heating scans of **Ph−P3OT−Br**, **PQ(EH)Br$_2$**, and **P3OT-PQ(EH)−P3OT** (10 °C min^{-1}).

Table 1. Properties of Ph−P3OT−Br (D), PQBr$_2$ (A) and D−A−D triblock copolymers

polymer	M_w,[a,b] (kg mol^{-1})	M_n,[b,c] (kg mol^{-1})	PDI[b,d]	DP[e,f]	T_m[g] (°C)	T_c[h] (°C)
Ph−P3OT−Br hexanes extract	3.1	2.7	1.2	12	176	157
Ph−P3OT−Br CHCl$_3$ extract	5.3	4.2	1.3	20	185	159
PQ(EH)Br$_2$	12.0	5.7	2.1	14	110	-
PQ(C8)Br$_2$	8.3	4.6	1.8	8	72 (br)	-
P3OT-PQ(EH)−P3OT	26.0	10.0	2.6	42	75 115	92
P3OT-PQ(C8)−P3OT	28.8	10.3	2.8	36	-	-

[a] Weight-average molecular weight (M_w). [b] Determined by gel permeation using polystyrene standards. [c] Number-average molecular weight (M_n). [d] Polydispersity index (PDI). [e] Degree of polymerization (aryl repeat units). [f] Determined by end group analysis. [g] Melting temperatures determined by a DSC scan rate of 10 °C.min^{-1}. [h] Recrystallization temperatures determined by a DSC scan rate of 10 °C.min^{-1}.

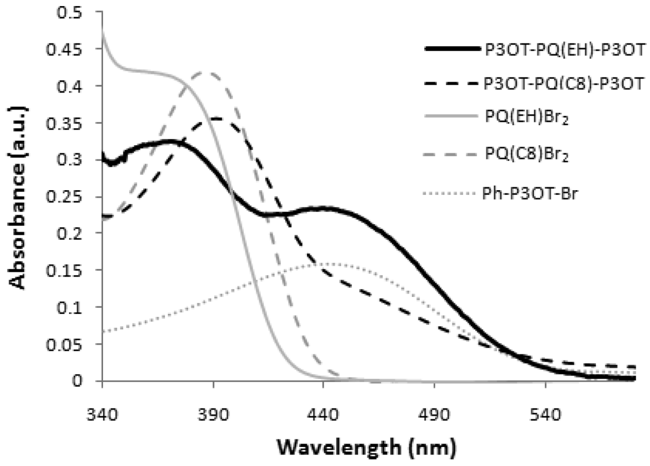

Figure 10. UV−visible absorption spectra in chloroform (5 mg/100 mL) for **Ph−P3OT−Br** (dotted line), **PQ(C8)Br$_2$** (gray dashed line), **PQ(EH)Br$_2$** (black dashed line), and D−A−D triblock copolymers **P3OT−PQ(C8)−P3OT** (gray solid line), and **P3OT−PQ(EH)−P3OT** (black solid line).

The thermal transition temperatures of the polymers prepared in this study were measured by differential scanning calorimetry (DSC) in a nitrogen atmosphere, Table 1. DSC heating scans of **Ph−P3OT−Br** and **PQ(EH)Br$_2$** and corresponding triblock copolymer are shown in Figure 9. The hexanes soluble fraction of **Ph−P3OT−Br** has a single endothermic peak on heating at 176 °C and a supercooled crystallization transition at 157 °C upon cooling. The melting transition of **PQ(EH)Br$_2$** occurs at 110 °C. The corresponding triblock copolymer, **P3OT-PQ-(EH)−P3OT** has two melting transitions at 75 and 115 °C, and one crystallization peak upon cooling at 92 °C. Depression of melting points of the separate components in other conjugated block copolymers has been previously observed.[44,45] Accordingly, the endothermic transitions of the triblock copolymer may correspond to melting of the **PQ(EH)** and **P3OT** segments, respectively. The triblock copolymer **P3OT-PQ(C8)−P3OT** does not show any thermal transitions, indicating that this polymer is largely amorphous.

The solution UV−visible absorption spectra of **PQBr$_2$**, **Ph−P3OT−Br**, and D−A−D triblock copolymers **P3OT−PQ(C8)−P3OT** and **P3OT−PQ(EH)−P3OT** are shown in Figure 10. The solution spectra were recorded for solution of the polymer in chloroform (5 mg/100 mL). The precursors for the polyquinioxaline blocks, **PQ(C8)Br$_2$** and **PQ(EH)Br$_2$** absorb at 392 and 376 nm, respectively. The telechelic poly(3-octylthiophene) bearing phenyl and α-bromothienyl termini absorbs at 450 nm. These absorptions are similar to previously reported values for related homopolymers.[18,43] The spectra of the D−A−D triblock copolymers display absorption bands that are similar to those of the constituent blocks. For example, the **P3OT−PQ(EH)−P3OT** triblock copolymer has absorption bands at 378 and 450 nm. The height of the absorbance band at 450 nm of **P3OT−PQ(EH)−P3OT** is smaller than that of the **Ph−P3OT−Br** homopolymer because there is less of the P3OT segment present in the triblock copolymer. As the block copolymer spectrum is, for the most part, a superposition of the homopolymer spectrum, there is no apparent ground state interaction between the donor and acceptor segments.

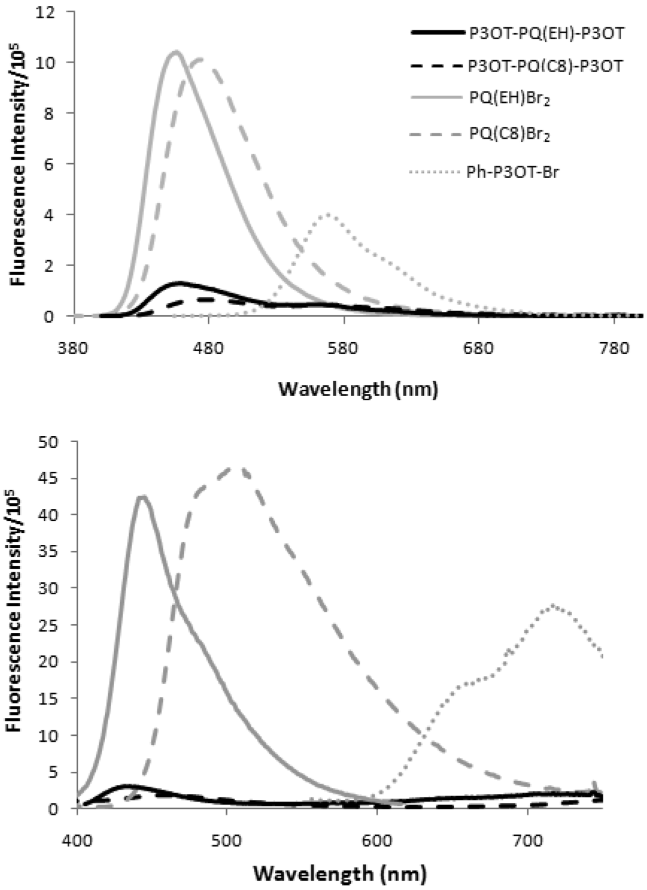

Figure 11. Fluorescence spectra of solutions (top; 5 mg/100 mL) and solid state (bottom; films cast from 15 mg/mL solutions in 1,4-dichlorobenzene) of **PQ(C8)Br$_2$** (dashed line), **Ph−P3OT−Br** (dotted line) and D−A−D triblock copolymers, **P3OT−PQ−P3OT**.

The solid state absorptions are broader and red-shifted for all of the materials (see Supporting Information). The absorption maxima for the homopolymers occur at 501 nm for **Ph−P3OT−Br**, at 396 nm for **PQ(C8)Br$_2$** and at 366 nm for **PQ(EH)Br$_2$**. The spectrum of the solid state D−A−D triblock **P3OT−PQ(C8)−P3OT** has two absorption transitions, at 490 and 407 nm, that may be ascribed to the donor and acceptor segments, respectively. Similarly, **P3OT−PQ(EH)−P3OT** has absorption transitions at 500 and 366 nm.

While the absorption spectra of the block copolymers have transitions that are similar to those of the constituent homopolymers, the fluorescence spectra have much more noticeable differences. The solution and thin film fluorescence spectra are shown in Figure 11. The emission of a solution of the precursor poly(3-octylthiophene) block occurs at 560 nm, and the emission of the poly(5,8-quinoxaline) precursors occur at 455 nm (C8 analogue) and 473 nm (EH), consistent with previously reported results for related homopolymers.[18,43] However, the emission spectra of the block copolymer shows almost complete quenching of the fluorescence, consistent with electron transfer from the donor to the acceptor segment. The solid state fluorescence spectra were measured on films prepared by casting 15 mg/mL of the polymers in 1,4-dichlorobenzene onto quartz slides. The emission maximum of poly(3-octylthiophene) occurs at 770 nm and that of the poly(5,8-quinoxaline)s occur at 507 nm (C8) and 443 (EH). As with the solution spectra, films

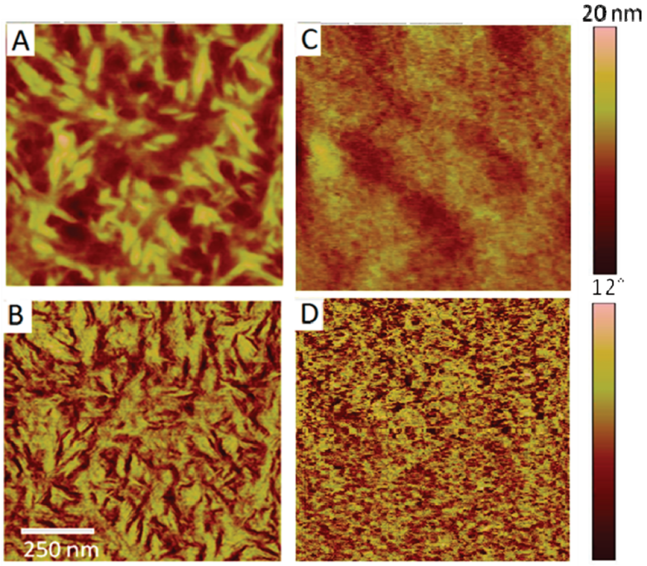

Figure 12. Tapping-mode atomic force microscopy (AFM) images of spin-coated thin films cast from chloroform onto ITO. **P3OT−PQ(EH)−P3OT**: A, height; B, phase. **P3OT−PQ(C8)−P3OT**: C, height; D, phase.

of the block copolymer show almost complete quenching of the fluorescence.

To investigate the morphology of the D−A−D triblock copolymers, thin films of **P3OT−PQ(EH)−P3OT** were cast from chloroform and dichlorobenzene. Atomic force microscopy height and phase images on the films are presented in Figure 12. The nanostructure apparent in these images may be attributed to phase separation of the poly(3-octylthiophene) segments and the poly(5,8-quinoxaline) segments. While the nanoscale phase separation of certain conjugated block copolymers may be ascribed to the presence of crystalline and amorphous blocks,[18,46] an alternate explanation in terms of π-stacking interactions has also been posited.[25] Accordingly, as with other block copolymers, the thermodynamically driven phase separation is a function of Flory−Huggins interaction parameters and does not strictly rely on the presence of crystalline and amorphous blocks. Films of homopolymer cast under the same conditions did not show such textures.

CONCLUSIONS

In conclusion, we have established new synthetic routes to a monofunctional, telechelic poly(3-octylthiophene) where the single bromine end group can be used as a functional handle in subsequent coupling reactions. This was achieved by CTCP of 2-bromo-3-octylthienylmagnesium iodide from a phenylnickel(II) initiator at 0 °C, and delaying quenching of the polymerization rather than precipitation as soon as the monomer has been consumed. Working at low temperature slows down the dissociative reductive elimination of nickel from the polymer during propagation, ensuring placement of phenyl groups at the initiated terminus of the chains in favor of competing chain transfer processes. The delay in quenching of the polymerization after consumption of the monomer allows time for reductive elimination of nickel and installation of the α-bromothienyl terminal functionality. The telechelic **Ph−P3OT−Br** block was coupled to a poly(5,8-quinoxaline) bearing boronic esters at each end to prepare a new class of D−A−D triblock copolymers with poly(3-octylthiophene) donor and poly(5,8-quinoxaline) acceptor blocks. The synthetic method established in this study to afford poly(3-octylthiophene) with the Ph/Th−Br combination of end groups might be applicable to the preparation of a broad array of new materials. Characterization of the D−A−D triblock copolymers in this study reveals efficient fluorescence quenching of the polymers in the solid state, supporting the occurrence of electron transfer.

EXPERIMENTAL SECTION

General Methods. All starting materials were purchased from commercial sources and used without further purification unless otherwise stated. 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, GA). NMR analysis was performed on a Bruker DSX 300 instrument using $CDCl_3$ as the solvent. Chemical shifts are referenced to internal tetramethylsilane. IR analyses were performed on a Nicolet 4700 FTIR with an ATIR attachment from Smart-Orbit Thermoelectronic Corporation. Ultraviolet−visible analysis was performed on a Shimadzu UV-2401PC spectrometer, and fluorescence spectroscopy was performed on a Shimadzu RF-5301PC spectrofluorophotometer. AFM scans were conducted using a Veeco Dimension V AFM. Thin film samples were prepared from dichlorobenzene and chloroform solutions (20 mg/mL and analyzed in tapping mode with a Nanosensors silicon AFM probe (model PPP-NCHR). Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA). 4,7-Dibromobenzo[*c*]-[1,2,5]thiadiazole (**1**),[47] $Ni(PPh_3)_4$,[48] and 2-bromo-5-iodo-3-octylthiophene[25] were prepared using previously reported methods. Synthesis of analogues **a** ($R = -C_6H_4-OC_8H_{17}$) are described below. Homologues **b** (*R* = 2-ethylhexyl) were synthesized using similar procedures unless otherwise stated. Spectral characterization of compounds **7** and **8** and homologue **b** is provided in Supporting Information.

1,2-Bis(4-(octyloxy)phenyl)ethane-1,2-dione, 3a. Potassium carbonate (15.2 g, 110 mmol) and tetrabutylammonium bromide (8.0 g, 25 mmol) were added to a solution of 1-bromooctane (15 mL, 88 mmol) and 1,2-bis(4-hydroxyphenyl)ethane-1,2-dione (10.6 g, 41.4 mmol) in anhydrous DMF (150 mL) under argon. The mixture was heated at 80 °C for 24 h, cooled and poured into H_2O (700 mL). The resulting mixture was filtered and the filtrate was recrystallized from ethanol to afford **3a** as a colorless solid (10.6 g, 52%): mp = 63−64 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, $^3J_{HH} = 8.7$ Hz, 4H, Ar C2−H), 6.93 (d, $^3J_{HH} = 8.7$ Hz, 4H, Ar C3−H), 4.02 (t, $^3J_{HH} = 6.6$ Hz, 4H, $-OCH_2-$), 1.74−1.84 (m, 4H), 1.28−1.47 (m, 20H), 0.88 (t, $^3J_{HH} =$ 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.52 (C═O), 164.43 (Ar C4), 132.31 (Ar C2), 126.00 (Ar C1), 114.65 (Ar C3), 68.42 (C−O), 31.74, 29.25, 29.16, 28.96, 25.89, 22.61, 14.07. IR (ATIR): 2916 (Ar C−H str.), 2844, 1664, 1597, 1573, 1508, 1463, 1421, 1251 (C−O str.), 1162, 1058, 1014, 956, 889, 842, 759, 649, 617 cm^{-1}. HRMS: calcd for $C_{30}H_{42}O_4$ = 466.3083; obsd = 466.3091; Δ = 1.7 ppm. Anal. Calcd: C, 77.21; H, 9.07. Found: C, 76.38; H, 8.90.

5,8-Dibromo-2,3-bis(4-(octyloxy)phenyl)quinoxaline, 4a. $NaBH_4$ (9 g, 238 mmol) was added in four equal portions 20 min apart to a solution of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (**1**) (6.1 g, 21 mmol) and $CoCl_2 \cdot 6H_2O$ (0.1 g, 0.4 mmol) in EtOH (100 mL) under argon. The solution was stirred for an additional 30 min and the solvent was removed under reduced pressure. The residue was taken up in H_2O (100 mL) and the mixture was neutralized with 10% HCl (50 mL) and extracted with CH_2Cl_2 (2 × 200 mL). The organic extracts were combined and the solvent was removed under reduced pressure to afford **2** as a colorless solid (3.5 g). ^1H NMR (300 MHz, $CDCl_3$): δ 6.16

(s, 2H), 3.37 (br s, 4H). The crude solid is unstable in light and air and was used immediately without further purification.

A solution of 3,6-dibromobenzene-1,2-diamine (**2**) (3.5 g, 13 mmol) and **3a** (5.0 g, 11 mmol) in acetic acid (200 mL) was heated to reflux for 24 h. The solution was cooled to room temperature and poured into H_2O (200 mL). The mixture was filtered and the filtrate was purified by column chromatography (30:70 v/v CH_2Cl_2:hexanes) to afford **4a** as a yellow solid (4.4 g, 56%), mp = 81−83 °C . ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (s, 2H, quinioxaline C−H), 7.65 (d, $^3J_{HH}$ = 8.7 Hz, 4H, phenyl C2−H), 6.87 (d, $^3J_{HH}$ = 8.7 Hz, 4H, phenyl C3−H), 3.99 (t, $^3J_{HH}$ = 6.6 Hz, 4H, $-OCH_2-$), 1.78−1.82 (m, 4H), 1.28−1.49 (m, 20H), 0.89 (t, $^3J_{HH}$ = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.41 (phenyl C4), 153.53 (quinoxaline C2 and C3), 138.95 (quinoxaline C1 and C4), 132.44 (quinoxaline C6 and C7), 131.63 (phenyl C2), 130.26 (phenyl C1), 123.38 (quinoxaline C5 and C8), 114.31 (phenyl C3), 68.05 (C−O), 31.79, 29.33, 29.21, 29.16, 26.00, 22.63, 14.09. IR (ATIR): 2912 (Ar C−H str.), 2846, 1600, 1512, 1468, 1377, 1242, 1173 (C−O str.), 985, 821, 717, 656, 540 cm^{-1}. HRMS: calcd for $C_{36}H_{44}Br_2N_2O_2$ = 694.1770; obsd = 694.1767; Δ = 0.4 ppm. Anal. Calcd: C, 62.07; H, 6.37; N, 4.02. Found: C, 61.81; H, 6.31; N, 4.21.

Monofunctional Telechelic Polythiophene, Ph−P3OT−Br. In a argon-filled glovebox, bromobenzene (1 mL, 1.5 g, 9.5 mmol) was added to a solution of $Ni(PPh_3)_4$ (1.3 g, 1.17 mmol) and anhydrous toluene (8 mL). The mixture was stirred overnight, and the solution turned from red to yellow. The mixture was filtered and the solid was washed with toluene (30 mL) to afford the arylnickel(II) initiator (**5**) as a yellow solid (0.5 g, 57%). In a separate oven-dried Schlenk flask, iPrMgCl (1 M in THF, 3.5 mL, 7.0 mmol) was added to a solution of 2-bromo-5-iodo-3-octylthiophene (2.8 g, 7.0 mmol) in THF (30 mL) at 0 °C. After 1 h, a solution of the phenylnickel(II) initiator (**5**) (0.10 g, 0.14 mmol) in THF (2 mL) was added to the reaction mixture. The mixture was stirred for 1 h at 0 °C and transferred to a freezer (−20 °C) for 12 h. Hexanes (20 mL) was added and the mixture was poured into MeOH (100 mL). The resulting precipitate was sequentially extracted in a Soxhlet extractor with acetone, hexanes and chloroform to afford **Ph−P3OT−Br** as a purple solid: the hexanes extracted fraction (350 mg, 26%); the chloroform extracted fraction (637 mg, 47%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (br s, 1H), 2.74−2.89 (m, 2H), 1.71−1.82 (m, 2H), 1.32−1.44 (m, 10H), 0.89−0.91 (m, 3H). IR (ATIR): 2922, 2850, 1662, 1563, 1509, 1456, 1377, 1055, 823, 754, 723, 661 cm^{-1}. GPC (THF, UV−vis detector): hexanes fraction, 2.4 kDa, PDI = 1.3; chloroform fraction, 2.9 kDa, PDI = 1.0.

Poly(2,3-(4-octyloxyphenyl)quinoxaline-5,8-diyl), PQ(C8)Br$_2$. In an argon-filled glovebox, $Ni(COD)_2$ (0.71 g, 2.6 mmol) was added to a Shlenk flask containing a solution of dibromide **4a** (1.5 g, 2.2 mmol), 2,2′-bipyridine (0.44 g, 2.8 mmol) 1,5-cyclooctadiene (1 mL, 8 mmol) in anhydrous *N*,*N*-dimethyformamide (25 mL). The mixture was stirred at 60 °C for 48 h, and then poured into MeOH (100 mL). The solution was filtered and the resulting gray precipitate was dissolved in $CHCl_3$ (50 mL) and the solution was stirred with 10% aqueous HCl (20 mL) for 30 min. The organic layer was separated and then stirred with 10% KOH (20 mL) for 30 min. The organic layer was separated and the polymer was precipitated by pouring the solution into MeOH (200 mL). The solution was filtered and **PQ(C8)Br$_2$** was obtained as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (br s, 2H, quinoxaline C−H), 6.60 (b, 4H, phenyl C−H), 3.7 (b, 4H, $-OCH_2-$), 1.54−1.87 (m, 4H), 1.15−1.42 (m, 20H), 0.87 (b, 6H). IR (ATIR): 2927, 2856, 1604, 1511, 1467, 1384, 1342, 1294, 1243, 1172, 1027, 977, 831, 736, 665, 592, 540 cm^{-1}. GPC (THF, UV−vis detector): 4.28 kDa; PDI = 1.93.

Poly(2,3-(2-ethylhexyl)quinoxaline-5,8-diyl), PQ(EH)Br$_2$. Polymerization of monomer **4b** (2.0 g, 3.9 mmol) was carried out according to the procedure provided above to afford **PQ(EH)Br$_2$** as a yellow solid (1.1 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (b, 2H, quinoxaline C−H), 2.79 (b, 4H, Ar−CH_2−), 1.92 (b, 2H, $-CH_2CH(CH_2)_2-$), 1.07−1.36 (m, 16H) 0.67−0.87 (m, 12H). IR (ATIR): 2954, 2921, 2854, 1580, 1460, 1377, 1308, 1205, 1172, 1094, 923, 827, 767, 726, 653, 567, 445 cm^{-1}. GPC (THF, UV−vis detector): 5.7 kDa; PDI = 2.1.

Boronate-Ester-Modified Poly(2,3-(4-octyloxyphenyl)quinoxaline-5,8-diyl), PQ(C8)−B(OR)$_2$. In a dry Schlenk flask under argon, bis(pinacolato)diboron (0.4 g, 1.6 mmol), potassium acetate (0.18 g, 1.8 mmol) and Pd(dppf)Cl_2 (0.06 g, 0.08 mmol) were added to a solution of **PQ(C8)Br$_2$** (0.67 g, 0.02 mols Br end groups) in anhydrous 1,4-dioxane (30 mL). The solution was stirred at 50 °C for 48 h, and then poured into MeOH (100 mL). The mixture was filtered and the residue was washed with MeOH (200 mL) to afford **PQ(C8)−B(OR)$_2$** as a yellow solid (0.60 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (b, 2H, quinoxaline C−H), 6.60 (b, 4H, phenyl C−H), 3.7 (b, 4H, $-OCH_2-$), 1.54−1.87 (m, 4H), 1.15−1.42 (m, 20H), 0.87 (b, 6H). IR (ATIR): 2924, 2852, 1600, 1512, 1471, 1382, 1342, 1294, 1249, 1170, 1027, 979, 831, 665, 592, 538 cm^{-1}.

Boronate-Ester-Modified Poly(2,3-(2-ethylhexyl)quinoxaline-5,8-diyl), PQ(EH)−B(OR)$_2$. Modification of **PQ(EH)Br$_2$** (0.52 g 0.014 mols of Br end group) was carried out according to the procedure provided above to afford **PQ(EH)−B(OR)$_2$** as a yellow solid (0.47 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): 8.14 (b, 2H, quinoxaline C−H), 2.79 (b, 4H, Ar−CH_2−), 1.92 (b, 2H, −C2 CH), 1.07−1.36 (m, 16H) 0.67−0.87 (m, 12H). IR (ATIR): 2954, 2921, 2854, 1580, 1460, 1377, 1308, 1248 (C−O str.), 1205, 1172, 1094, 923, 827, 767, 726, 653, 567, 445 cm^{-1}.

ABA Triblock Copolymer, P3OT−PQ(C8)−P3OT. K_2CO_3 (2 M, aq, 5 mL) was added to a solution of **PQ(C8)−B(OR)$_2$** (0.55 g) and hexanes-soluble **Ph−P3OT−Br** (0.61 g) in THF (20 mL), and the mixture was degassed by freeze−pump−thaw (2 × 15 min cycles). $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol) was added and the solution was heated to 60 °C for 3 d. The mixture was poured into MeOH (100 mL) and filtered. The resulting solid was sequentially extracted in a Soxhlet extractor with MeOH, acetone, hexanes and $CHCl_3$. The solvent from the $CHCl_3$ fraction was removed under reduced pressure to afford **P3OT−PQ(C8)−P3OT** as a purple solid (0.62 g, 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.56 (br s, quinoxaline C−H), 7.24 (br s, thiophene C−H), 6.85 (m, 4H, phenyl C−H), 4.03 (m, $-OCH_2-$), 3.06 (m, Th−CH_2−), 1.61−1.76 (m), 1.10−1.41 (m), 0.73−0.89 (m). IR (ATIR): 2924, 2854, 1604, 1509, 1467, 1384, 1342, 1294, 1240, 1170, 1112, 1025, 979, 831, 723, 663, 632, 590, 536 cm^{-1}. GPC (THF, UV−vis detector): 10.3 kDa; PDI = 2.8.

ABA Triblock Copolymer, P3OT−PQ(EH)−P3OT. Coupling of hexanes soluble **Ph−P3OT−Br** (0.38 g) and **PQ(EH)−B(OR)$_2$** (0.46 g) was carried out according to the procedure provided above to prepare **P3OT−PQ(EH)−P3OT** and the product was isolated as a purple solid (0.55 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (bs, quinoxaline C−H), 6.98 (s, thiophene C−H), 2.80 (m, Th−CH_2−), 1.83−1.95 (m), 1.56−1.69 (m), 1.06−1.44 (m), 0.66−0.93 (m). IR (ATIR): 2956, 2927, 2856, 1495, 1379, 1261, 1095, 1018, 923, 800, 725, 696, 673, 622, 541, 443 cm^{-1}. GPC (THF, UV−vis detector): 10.0 kDa; PDI = 2.6.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental procedures and spectroscopic data, ^{1}H NMR of block copolymers, IR spectra, solid state UV−visible absorption spectra, and wide-angle X-ray diffractograms. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: david.collard@chemistry.gatech.edu.

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