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Chalcogen Bridged Thieno- and Selenopheno[2,3-d:5,4-d']bisthiazole and Their Diketopyrrolopyrrole Based Low-Bandgap Copolymers

Dhananjaya Patra,[†][®] Jaehyuk Lee,[‡] Somnath Dey,[†] Jongbok Lee,[§][®] Alexander J. Kalin,[§] Anjaneyulu Putta,[†] Zhuping Fei,^{||} Thomas McCarthy-Ward,^{||} Hassan S. Bazzi,[†] Lei Fang,[§][®] Martin Heeney,^{||}[®] Myung-Han Yoon,[‡] and Mohammed Al-Hashimi^{*,†}[®]

[†]Department of Chemistry, Texas A&M University at Qatar, P.O. Box 23874, Doha, Qatar

*Materials Science and Engineering, Gwangju Institute of Science and Technology, 123 Cheomdan-Gwagiro, Buk-gu, Gwangju 61005, South Korea

[§]Department of Chemistry, Texas A&M University, 3255 TAMU, College Station, Texas 77845-3255, United States

Department of Chemistry and Centre for Plastic Electronics, Imperial College London, Exhibition Road, London SW7 2AZ, U.K.

Supporting Information

ABSTRACT: We report the synthesis and characterization of four novel small bandgap copolymers incorporating the electron-deficient thieno [2,3-d:5,4-d'] bisthiazole and selenopheno[2,3-d:5,4-d']bisthiazole building blocks with a series of electron-deficient diketopyrrolopyrole units. The four resultant copolymers were synthesized via palladium Stille cross-coupling reaction, and their optical, thermal stability, electrochemical, and field-effect charge transport properties were investigated. All copolymers showed low optical bandgaps (1.53-1.56 eV); in addition, X-ray diffraction on solution-cast films revealed that the selenium-containing copolymers exhibit higher crystallinity compared to their thiophene counterparts.

INTRODUCTION

 π -Conjugated polymers are interesting materials that are extensively studied due to their tunable optoelectronic properties, synthetic simplicity, and modularity which continue to provide a unique value for a host of applications including organic field-effect transistors (OFETs),¹ organic light-emitting diodes (OLEDs),^{2,3} polymer solar cells (PSCs),⁴⁻⁶ photodiodes,⁷ and spintronics.⁸

The development of functional monomers via the commonly used transition-metal-catalyzed polymerizations such as Suzuki, Stille, and direct heteroarylation⁹ unlocks the potential to design many new building blocks. Specifically, careful modulation of the highest occupied and lowest unoccupied molecular orbitals (HOMO/LUMO) is key to engineering low-bandgap polymers. A common approach to lowering the optical bandgap between the HOMO and LUMO is using alternating electron-rich donors and electron-deficient acceptors as building blocks whose frontier molecular orbital energy levels can be easily tuned, ensuring effective charge transport and, moreover, promoting intramolecular interaction to enhance backbone ordering.¹⁰

One building block of particular interest that has shown to decrease the LUMO energy level is the electron-deficient bisthiazole unit.¹¹⁻¹⁶ Most of the research to date on conjugated copolymers based on bisthiazoles has been dedicated to either the main-chain or side-chain engineering of the electron-deficient unit.^{11,17-19} In addition, our research group and others have reported the effects of introducing a nitrogen atom to bridge the thiazole units to afford the fused building block pyrrole[2,3-d:5,4-d']bisthiazole (PBTz) (Figure 1).²⁰⁻²³ We note here our gratitude to Rasmussen et al.²³ for highlighting that our earlier publications had used the incorrect IUPAC name. The bridged architecture has significant effects on the electronic and structural properties of the polymer main chain. Thus, one way to further tune the electrochemical, optical, and charge transport properties of the polymer is to modify the bridging heteroatom in the heterocycle.

In recent years, several heteroatom-bridged bithiophene²⁴⁻²⁸ derivatives (Figure 1, DTP, DTT, DTG, DTS, DTAs, and CPDT) have been comprehensively studied as building blocks of conjugated polymers. Although the selenium bridged bithiophene has not been reported to the best of our

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Figure 1. (a) Chemical structures of some bridge monomers in the literature and (b) monomers reported in this work and previous work.

Scheme 1. Synthetic Route to Intermediates 1 and 2 and Dibromothieno[2,3-d:5,4-d']bisthiazole (BTzS 8) and Dibromoselenopheno[2,3-d:5,4-d']bisthiazole (BTzSe 9) Building Blocks



Scheme 2. Synthetic Route to P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) Copolymers by Stille Cross-Coupling Polymerization



knowledge, other reports suggest that replacing sulfur with the heavier and less electronegative selenium atom leads to stronger intermolecular interactions and a higher degree of rigidity and as a result extends the absorption spectrum toward the near-infrared region.^{29–32} Similarly we recently reported a series of vinylene copolymers containing 3-dodecylthiophene, selenophene, and tellurophene in which we found that the inclusion of the heavier heteroatoms resulted in a significant reduction in optical bandgap in comparison to the thiophene counterpart, mainly as a result of stabilization of the polymer LUMO.³³ Inspired by these works, we were interested to prepare heteroatom bridged bisthiazole monomers, which are unknown to the best of our knowledge.

Here we describe the first synthesis of the novel electrondeficient thieno[2,3-d:5,4-d'] bisthiazole BTzS and selenopheno[2,3-d:5,4-d']bisthiazole BTzSe building blocks. The newly designed bisthiazole moieties were copolymerized with a series of electron-deficient diketopyrrolopyrole (DPP) units having long and branched side chains on the two lactam rings flanked by either bisthiophene (BT) or thieno[3,2-b]thiophene (TT). The optical, physical, electrochemical, and field-effect charge transport properties of the four resultant copolymers P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) were characterized. All copolymers showed low optical bandgaps (1.53–1.56 eV), and the nature of the bridged heteroatom was shown to have a subtle impact on the polymer ionization potential. X-ray diffraction on solution-cast films suggested that the selenium-containing copolymers P(DPPBT-BTz-Se) and P(DPPTT-BTz-Se) exhibited higher crystallinity compared to their

Table 1. Molecular Weights and Optical and Electrochemical Properties of P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) Copolymers

					$\lambda_{ m max}$					
polymers	$M_{\rm w}~({\rm kDa})$	$M_{\rm n}^{\ a}$ (kDa)	\overline{D}^{a}	$T_{\rm d}$ (°C)	solution ^b	film ^c	$HOMO^d$ (eV)	$LUMO^{d}$ (eV)	$E_{g}^{ec e}$ (eV)	$E_{g}^{optf}(eV)$
P(DPPBT-BTz-S)	36.5	6.8	5.4	316	425, 654	465, 656	-5.15	1.56	1.56	1.51
P(DPPTT-BTz-S)	46.6	7.8	4.1	330	426, 624	430, 628	-5.13	1.55	1.55	1.52
P(DPPBT-BTz-Se)	41.6	6.7	4.2	362	441, 683	474, 686	-5.11	1.55	1.55	1.45
P(DPPTT-BTz-Se)	41.1	10.5	3.9	368	427, 639	435, 639	-5.10	1.53	1.53	1.50

^{*a*}Determined by gel permeation chromatography (against polystyrene standards) in chlorobenzene at 80 °C. ^{*b*} λ_{max} in chloroform dilute solution. ^{*c*}Spin-coated from chloroform solution onto a glass surface. ^{*d*} $E_{HOMO}/E_{LUMO} = [-(E_{onset} - E_{onset}(FC/FC^+vsAg/Ag^+)) - 4.8] eV, where 4.8 eV is the energy level of ferrocene below the vacuum level and the formal potential <math>E_{onset}(FC/FC^+vsAg/Ag^+)$ is equal to 0.45 V. ^{*e*}Electrochemical bandgap: $E_g^{ec} = E_{ox/onset} - E_{red/onset}$. ^{*f*}Optical bandgap: $E_g^{opt} = 1240/\lambda_{edge}$.



Figure 2. Normalized UV-vis absorption spectra of P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se): (a) dilute solutions in CHCl₃ and (b) thin films on quartz surfaces at room temperature.

thiophene counterparts P(DPPBT-BTz-S) and P(DPPTT-BTz-S).

RESULTS AND DISCUSSION

Synthesis of Monomers, Polymers, and Characterization. The general synthetic route of the monomers is depicted in Scheme 1. Precursors 1 and 2 were synthesized according to reported literature procedures with slight modifications.³⁴ The detailed synthesis of 4,4'-dibromo-2,2'bis(triisopropylsilyl)-5,5'-bithiazole (3) is reported in our previously published work.^{16,20,23}

The new comonomers 8 and 9 were synthesized in three steps from monomer 3. Stille coupling of 3 with precursors 1 and 2 in toluene at 170 °C afforded compounds 4 and 5 in moderate yields (35-36%). Subsequent deprotection of the triisopropylsilyl (TIPS) groups using TBAF gave 6 and 7. Treatment of compounds 6 and 7 with N-bromosuccinimide (NBS) in DMF afforded 2,6-dibromothieno[2,3-d:5,4-d']bisthiazole (8) and 2,6-dibromoselenopheno[2,3-d:5,4-d']bisthiazole (9) as yellow solids in 52% and 56% yields (Scheme 1).

As depicted in Scheme 2, P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) copolymers were synthesized via microwave-assisted Stille coupling polymerization of dibrominated monomers 8 and 9 with the corresponding distannylated DPPBT (10) and DPPTT (11) in the presence of Pd(PPh₃)₄ and tri(*o*-tolyl)phosphine in anhydrous chlorobenzene at 180 °C. Purification of the four copolymers was performed by sequential Soxhlet extraction with methanol, acetone, hexane, and dichloromethane to remove low molecular weight oligomers and catalyst residues. The chloroform soluble fraction was concentrated in volume, and the copolymers were collected by precipitation in methanol to afford blue solids in moderate 45-58% yields. The resultant low- M_w copolymers displayed good solubility in chloroform at room temperature.

Number-average (M_n) and weight-average molecular weight (M_w) were determined by GPC in chlorobenzene at 80 °C. The copolymers P(DPPBT-BTz-S), P(DPPTT-BTz-S), P-(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) exhibited modest M_n in the range 6.71–10.53 kDa, with D in the range 3.9–5.4, as listed in Table 1. All copolymers have relatively low M_w and are in the oligomer range. The relatively large polydispersity indexes of the copolymers can be attributed to the aggregation in solution at low temperatures. In a similar system (fused thiophene–diketopyrrolopyrrole) it has been found that to obtain nonaggregated polymers elevated temperatures of 200 °C are required.³⁵

The relatively low molecular weights may result from the difficulty in obtaining the trimethylstanyl monomers in high purity. Such tin monomers have a tendency to decompose upon silica during attempted purification. The commercially available monomers **10** and **11** had a low purity. Both monomers were oils, and our attempts at recrystallization were not successful. We did attempt to purify by column chromatography using ALOX, but this led to further loss of the stannyl groups.

Thermal Properties. The thermal stability of the copolymers was evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) depicted

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Figure 3. (a) Cyclic voltammograms of P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) as thin films (scan rate: 50 mV s^{-1}). (b) HOMO and LUMO energy levels of the copolymers.

in Figures S1 and S2. The TGA curves reveal that all the copolymers are thermally stable with a degradation temperature (T_d) of 5% weight loss greater than 300 °C under a nitrogen atmosphere at a heating rate of 10 °C/min (Figure S1). Interestingly, copolymers containing the selenium heteroatom resulted in slightly higher thermal stability than the sulfur-containing counterparts. We note that the high thermal stability should be adequate for their applications in optoelectronic devices. The copolymers all showed a glass transition temperature (T_g) over 250 °C calculated from the DSC curve. However, the copolymers did not show any endothermic or exothermic peaks (Figure S2), such as melting or crystallization peaks when heated or cooled, perhaps as a result of the extended backbone.

Optical Properties. The UV-vis absorption spectra of all four copolymers P(DPPBT-BTz-S), P(DPPTT-BTz-S), P-(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) were recorded at room temperature both in dilute chloroform solution and as thin films spin-coated onto quartz substrates (Figure 2). The maximum absorbance (λ_{max}) in solution and solid state and the optical bandgaps (E_g^{opt}) are summarized in Table 1. The absorption spectra of all the copolymers in solution exhibited two main absorption bands: one in the range 350-500 nm, which is attributed to localized $\pi - \pi^*$ transitions, and a second band having a vibronic shoulder in the range of 500-820 nm in the long wavelength region. The substitution of the sulfur heteroatom in P(DPPBT-BTz-S) and P(DPPTT-BTz-S) with selenium in P(DPPBT-BTz-Se) and P(DPPTT-BTz-Se) leads to a red-shift of λ_{max} of 29 and 15 nm, respectively. All the four copolymers exhibit a small red-shifted absorption in the thin solid films (550-870 nm) compared to the chloroform solution. The red-shift is likely a result of backbone planarization in the solid state.

For the thin films, comparison of the sulfur bridged polymers P(DPPBT-BTz-S) and P(DPPTT-BTz-S) to the selenium bridged P(DPPBT-BTz-Se) and P(DPPTT-BTz-Se) shows a red-shift of λ_{max} of 30 and 11 nm, in agreement with the solution studies. The red-shift can be attributed to the electronic effect of the heteroatom. Thus, increasing the size of the heteroatom from sulfur to selenium is one way to red-shift the copolymers to a longer wavelength. The optical bandgaps (E_g^{opt}) of P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) thin film were estimated as

1.51, 1.52, 1.45, and 1.50 eV from the absorption onset as shown in Table 1. As expected, the selenium-containing copolymers exhibited smaller bandgaps than their sulfur counterparts, which can be explained due to the decrease in the aromaticity as the size of the heteroatom increases.³⁶

Electrochemical Properties. The ionization and reduction potentials of the copolymers were determined using cyclic voltammetry (CV) as depicted in Figure 3a. All four copolymers underwent quasi-reversible oxidation in the positive potential range and either quasi-reversible P-(DPPBT-BTz-S) and P(DPPBT-BTz-Se) or irreversible reduction in the negative potential range. The onset oxidation potentials (E_{ox}) of P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) were found to be 0.80, 0.78, 0.76, and 0.75 V vs Ag/Ag⁺, while the onset reduction potentials (E_{red}) were -0.76, -0.77, -0.79, and -0.78 V vs Ag/Ag⁺, respectively.

The LUMO energy levels, as calculated from reduction onsets for the copolymers P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se), were very similar at -3.59, -3.58, -3.56, and -3.57 eV, respectively. The HOMO energy levels of the copolymers were calculated from the onset oxidation potential and are -5.15, -5.13, -5.11, and -5.10 eV as shown in Figure 3b and Table 1. The calculated electrochemical bandgaps were approximately 1.56 eV for P(DPPBT-BTz-Se), 1.55 eV for P(DPPTT-BTz-Se), 1.55 eV for P(DPPTT-BTz-Se). The electrochemical bandgaps of the copolymers are well matched with their optical bandgaps within the experimental error.

Overall, it can be seen that replacing the heteroatom from sulfur to selenium in the bridged bisthiazole unit only has a subtle effect on the HOMO and LUMO energy levels of the resultant copolymers. The subtle effect likely stems from the relatively minor percentage component the heteroatom makes to the overall conjugated polymer backbone. Nevertheless, the trend observed for the HOMO and LUMO energy levels is in agreement with other reports on selenium-containing copolymers.³⁷

X-ray Diffraction and Surface Morphology. To gain insight into the film morphology and supramolecular organization of the copolymers, X-ray diffraction (XRD) measurements were performed on drop-cast polymer thin



Figure 4. (a) X-ray diffraction patterns and (b–e) AFM topography images of copolymers P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se,) and P(DPPTT-BTz-Se) and AFM topography phase images of the copolymer films P(DPPBT-BTz-S) (b), P(DPPTT-BTz-S) (c), P(DPPBT-BTz-Se) (d), and P(DPPTT-BTz-Se) (e) as cast films at 250 °C.



Figure 5. Transfer and output characteristics of OTFTs with P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se). (a) A schematic of bottom gate-top contact OTFT structure. (b) Transfer characteristics and (c) output characteristics of P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se). Black curves are drain current, and red curves are (drain current)^{1/2}.

films (Figure 4a). The four copolymers are all characterized by a diffraction peaks around $2\theta = 4.7^{\circ} - 4.8^{\circ}$, which is suggestive

of lamellar type ordering with an interchain distance of around 18-19 Å as well as broad diffraction peaks, which we assign to

polymers	annealing temp (°C)	channel length (μ m)	channel width (μ m)	$\mu_{ m h,lin}$, (cm ² V ⁻¹ s ⁻¹)	$\mu_{\rm h,satr}~({\rm cm}^2~{ m V}^{-1}~{ m s}^{-1})$	$V_{\rm th}$ hole (V)	$I_{\rm on}/I_{\rm off}^{\ a}$
P(DPPBT-BTz-S)	250	50	500	2.1×10^{-3}	4.3×10^{-3}	-10	2.5×10^{4}
P(DPPTT-BTz-S)	250	50	500	6.2×10^{-3}	9.5×10^{-3}	-10	3.0×10^4
P(DPPBT-BTz-Se)	250	50	500	1.7×10^{-4}	3.8×10^{-4}	-8.5	1.0×10^{4}
P(DPPTT-BTz-Se)	250	50	500	5.1×10^{-3}	1.9×10^{-2}	-3.5	1.0×10^{1}
${}^{a}I_{\rm on}/I_{\rm off}$ refers to the	e on-to-off current at	the max hole mobil	lity.				

Table 2. Summary of the OFET Charge Carrier Mobilities in Hole for Copolymers P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se)

 $\pi-\pi$ stacking. All polymers exhibit a similar $\pi-\pi$ stacking distance of 3.5 Å. In the case of the selenium-containing copolymers P(DPPBT-BTz-Se) and P(DPPTT-BTz-Se), the diffraction peaks showed slightly higher crystalline features compared to the sulfur-containing copolymers P(DPPBT-BTz-S) and P(DPPTT-BTz-S), which exhibited a second (200) and third (300) order lamellar packing features (2θ values around 9.52° and 14.28°).

The surface morphology of the four copolymer thin films was investigated using atomic force microscopy (AFM). Figure 4b-e illustrates the tapping-mode AFM images for P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P-(DPPTT-BTz-Se) prepared by spin-casting from chloroform solution onto SiO₂ substrates. All of the polymer films exhibited finely aggregated surfaces, and when thermally annealed at 250 °C, the surface roughness slightly increased. The average root-mean-square (rms) roughness values after annealing are 0.43, 0.49, 0.41, and 0.34 nm for the films of P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se), respectively. In addition, P(DPPTT-BTz-Se) copolymer thin film had a slightly smaller rms roughness value (0.34 nm) in the series, which formed interconnected nanoscale granules, resulting in low surface roughness.

Field-Effect Transport. The carrier mobilities were studied using organic thin film transistors (OTFTs) with a bottom-gate top-contact (BGTC) device configuration on ptype silicon wafer substrate as the gate electrode and SiO_2 (300 nm) layer as the gate dielectric (Figure 5a). A self-assembled monolayer of hexamethyldisilazane (HMDS) was deposited on SiO₂ to improve the device performance by reducing the trapping of charge in the interface between the dielectric layer and the semiconductor layer as well as potentially aiding the alignment of the polymers. Films were formed by spin-coating followed by a two-step heat treatment. First, preannealing at relatively low temperature (80 °C, 5 min) was performed to remove any remaining solvent, and then postannealing at a higher temperature (250 $^{\circ}$ C, 5 min) was performed to improve the device performance by the alignment of the semiconducting polymeric layer.

Figure 5 shows the typical transfer and output characteristics curves of the four copolymers, and the mobilities are summarized in Table 2. All the copolymers exhibit p-type characteristics in the HMDS-treated devices. The as-cast thin film of semiconducting copolymers P(DPPBT-BTz-S), P-(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) exhibited saturation mobilities of 4.3×10^{-3} , 9.5×10^{-3} , 3.8×10^{-4} , and 1.9×10^{-2} cm² V⁻¹ s⁻¹, respectively, with negligible hysteresis. We note that there is some leakage current in the low-voltage region of the output characteristic. This phenomenon occurs in an OTFT with the unpatterned semiconducting layers and causes an increase in the off current

due to parasitic current from the OTFT channel to the gate electrode edges.

Among the four copolymers P(DPPTT-BTz-Se) was found to exhibit the highest hole mobility and P(DPPBT-BTz-Se) the lowest hole mobility in OTFTs in comparison to the others. Given the similar bandgap and thin-film crystallinity, the highest and low mobilities of P(DPPTT-BTz-Se) and P(DPPBT-BTz-Se) are likely due to their different molecular weights, with the higher weight polymer exhibiting the best performance. In addition, in both sets of copolymers the DPPTT comonomers consistently gives higher performance than the corresponding DPPBT copolymers, in agreement with early studies.³⁸ Moreover, the hole mobility of the selenium copolymer with the DPPTT unit is double $(1.9 \times 10^{-2} \text{ cm}^2)$ V^{-1} s⁻¹) that of the copolymer with DPPBT (3.8 × 10⁻⁴ cm²) V^{-1} s⁻¹) moiety. Furthermore, the hole mobility of the corresponding selenium bridged copolymer P(DPPTT-BTz-Se) is improved by 1.5-fold over that of their corresponding sulfur-based copolymer P(DPPTT-BTz-S).

In summary, we have synthesized four novel bisthiazole-DPPbased copolymers P(DPPBT-BTz-S), P(DPPTT-BTz-S), P-(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) via the Stille coupling reaction and investigated the influence of changing the chalcogen heteroatom from sulfur to selenium. The copolymers were found to have small optical bandgaps and good thermal stability. The influence of the bridging chalcogen is found to be subtle, with a small reduction in optical bandgap observed. All four copolymers exhibited p-type semiconducting behavior in transistor devices, with a highest hole mobility of 1.9×10^{-2} cm² V⁻¹ s⁻¹ observed for P(DPPTT-BTz-Se). Further studies are currently underway to optimize the properties and device characteristics for this class of conjugated materials.

EXPERIMENTAL SECTION

General Procedures. All chemicals and solvents were purchased in reagent grade from Aldrich and Solamer, except for $Pd(PPh_3)_{4,r}$, which was obtained from Strem Chemicals Inc. Tetrahydrofuran (THF) and toluene were distilled over Na/benzophenone; all reagents were used as received. 4,4'-Dibromo-2,2'-bis-(triisopropylsilyl)-5,5'-bithiazole1 (3) was synthesized as from a reported procedure.¹⁶ 2,5-Bis(2-octyldodecyl)-3,6-bis(5'-(trimethylstannyl)-[2,2'-bithiophen]-5-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4dione (10) and 2,5-bis(2-octyldodecyl)-3,6-bis(5-(trimethylstannyl)thieno[3,2-*b*]thiophen-2-yl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4dione (11) were purchased from Solamer.

Measurements and Characterization. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker 400 MHz or DRX500 NMR spectrometers at 22 °C, using chloroform-*d* as solvent and the residual chloroform as the internal standard (7.26 ppm). Flash chromatography (FC) was performed on silica gel (Merck Kieselgel 60 F254 230–400 mesh) unless otherwise indicated. Thin

layer chromatography (TLC) was performed on Merck aluminumbacked plates precoated with silica (0.2 mm, 60 F254). Mass spectra were obtained using gas chromatography-mass spectrometry (GCMS, Shimadzu GCMS-QP2010). Elemental analyses were performed on a PerkinElmer 2400 Series II CHNS/O analyzer. The thermal stability of the polymers was evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) analyses. Number-average (M_n) and weight-average (M_w) molecular weights were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. UV-visible (UV-vis) absorption spectra were recorded in dilute chloroform solutions (10⁻⁶ M) on a PerkinElmer Lambda 950 spectrophotometer. Thin films for UV-vis measurements were spincoated on a glass substrate from chloroform solutions with a concentration of 5 mg/mL. Cyclic voltammetry (CV) measurements were performed using a BAS 100 electrochemical analyzer with a standard three-electrode electrochemical cell in a 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF₆) solution (in acetonitrile) at room temperature with a scanning rate of 100 mV/s. During the CV measurements, the solutions were purged with nitrogen for 30 s. In each case, a carbon working electrode coated with a thin layer of copolymers, a platinum wire as the counter electrode, and a silver wire as the quasi-reference electrode were used, and the Ag/AgCl (3 M KCl) electrode served as a reference electrode for all potentials quoted herein. The redox couple of the ferrocene/ ferrocenium ion (Fc/Fc^+) was used as an external standard. The corresponding highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were calculated using E_{oxd}^{onset} and E_{red}^{onset} for experiments in solid films of polymers, which were performed by drop-casting films with the similar thickness from THF solutions (ca. 5 mg/mL). The onset potentials were determined from the intersections of two tangents drawn at the rising currents and background currents of the CV measurements.

Transistor Fabrication and Characterization. Organic thin film transistors (OTFTs) were fabricated as bottom gate-top contact configuration. SiO_2 (300 nm)/P²⁺-Si wafer substrate (Taewon Scientific, South Korea) was cleaned by deionized water, acetone, and isopropanol. Then hexamethyldisilazane (HMDS) was coated by placing clean silicon substrates in a chamber saturated with HMDS vapor for 24 h at normal temperature and pressure (reference). The HMDS coated substrates were placed on a hot plate at 130 °C for 30 min to remove unreacted HMDS molecules (reference). The substrates were spin-coated by semiconductor solutions with chloroform (5 mg/mL) as follows in a N2 atmosphere: (1) 1000 rpm for 5 s, (2) 5000 rpm for 30 s, and (3) 1000 rpm for 5 s. Then the coated substrates were annealed on a hot plate at 80 °C for 5 min and at 250 °C for 30 min sequentially. Au source and drain electrodes (thickness: 40 nm; channel length and width: 50 and 500 μ m) were deposited using a thermal evaporator, and electrical performance of the OTFTs was characterized by using a Keithley 4200-SCS (Keithley, USA) with a probe station (MS-Tech, South Korea).

Synthesis of Monomers. 1,1,1,3,3,3-Hexabutyldistannathiane (1).³⁴ A solution of tributyltin chloride (28.5 g, 87.4 mmol) in THF (174 mL) was added to a solution of sodium sulfide nonahydrate (Na₂S·9H₂O) (10.5 g, 175 mmol) in deionized water (34.8 mL). Some additional deionized water (17.4 mL) was used to transfer the remaining Na₂S·9H₂O to the flask. The reaction mixture was stirred at 85 °C for 6 h. The reaction mixture was allowed to cool to room temperature, and the organic layer was evaporated under vacuum. The residue was extracted with Et₂O, dried over anhydrous magnesium sulfate, and evaporated to give a colorless oil (21.8 g, 81%) and was used without further purification. ¹H NMR (CDCl₃): δ 1.58–1.54 (m, 12H), 1.36–1.31 (m, 12H), 1.09–1.05 (m, 12H), 0.91 (t, 18H, J = 7.2 Hz).

1,1,1,3,3,3-Hexabutyldistannaselenane (2).³⁴ To selenium powder (2.07 g, 26.2 mmol), sodium metal pieces (1.21 g, 52.4 mmol) and naphthalene (0.6 g, 4.7 mmol) were added under an argon atmosphere, and the reaction mixture was degassed for 10 min. Dry THF (250 mL) was added, and the reaction mixture was heated to reflux for 24 h. The pale-brown suspension was cooled to 0 °C, tributyltin chloride (17.1 g, 52.5 mmol) was added, and the reaction mixture was stirred for another 24 h. Toluene (100 mL) was then added to the crude mixture. The residue was passed through a plug of silica, and the solvent was removed. The residue was passed through a second plug of silica containing potassium fluoride (8:2 ratio) to yield the target product as a pale yellow oil (11.4 g, 68%). ¹H NMR (CDCl₃): δ 1.58–1.54 (m, 12H), 1.37–1.30 (m, 14H), 1.14–1.10 (m, 10H), 0.94 (t, 18H, *J* = 7.2 Hz).

2,6-Bis(triisopropylsilyl)thieno[2,3-d:5,4-d']bis(thiazole) (4). To a 20 mL sealed microwave vial, compound 1 (0.47 g, 0.78 mmol), 4,4'dibromo-2,2'-bis(triisopropylsilyl)-5,5'-bithiazole (3)¹⁶ (1.0 g, 1.57 mmol), Pd(PPh₃)₄ (0.72 mg, 4 mol %), and dry toluene (4 mL) were added, and the reaction mixture was purged with argon for 20 min. The mixture was then heated to 170 °C in an oil bath overnight. After cooling the reaction mixture to room temperature, water (5 mL) was added, and the layers were extracted using dichloromethane (3×25) mL). The combined organic fractions were dried over MgSO₄, filtered through a silica plug, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel with hexanes/ dichloromethane (3:1) to afford a white solid (0.29 g, 36%). ¹H NMR (400 MHz, CDCl₃): δ 1.56–1.49 (septet, 6H, J = 8.0 Hz), 1.18–1.17 (d, 36H). ¹³C NMR (100 MHz, CDCl₃): δ 172.2, 160.2, 132.4, 129.9, 123.9, 18.5, 11.7. GC-MS calculated for $[C_{24}H_{42}N_2S_3Si_2]$ 510.96; found 510.90. ESI-MS m/z calcd for $C_{24}H_{43}N_2Si_2S_3$ (M + H)⁺ 511.2127; found 511.2118.

2,6-Bis(triisopropylsilyl)selenopheno[2,3-d:5,4-d']bis(thiazole) (5). Compound 5 was synthesized according to the same procedure for 4 with the respective monomer to afford a white solid (0.31 g, 36%). ¹H NMR (400 MHz, CDCl₃): δ 1.54–1.46 (septet, 6H, J = 8.0 Hz), 1.18–1.70 (m, 36H). ¹³C NMR (100 MHz, CDCl₃): δ 171.7, 158.9, 125.2, 18.5, 11.8. GC-MS calculated for [C₂₄H₄₂N₂S₂SeSi₂] 558.14; found 558.10.

Thieno[2,3-d:5,4-d']*bis*(*thiazole*) (6). To a solution of 4 (1.9 g, 3.71 mmol) in dry THF (10 mL) was added TBAF (14.87 mL, 14.87 mmol, 1 M THF). The reaction mixture was stirred at room temperature for 4 h, after which water was added and the residue was extracted using chloroform (3 × 15 mL). The combined organic fraction was washed with brine and water, dried over MgSO₄, and concentrated under reduced pressure to afford compound 6 as a pale yellow solid (0.50 g, 70%). ¹H NMR (400 MHz, CDCl₃): δ 8.91 (*s*, 2H).¹³C NMR (100 MHz, CDCl₃): δ 157.6, 153.1, 121.4. GC-MS calculated for [C₆H₂N₂S₃] 197.92; found 197.90. ESI-MS *m*/*z* calcd for C₆H₃N₂S₃ (M + H)⁺ 198.94; found 198.94.

Selenopheno[2,3-d:5,4-d']bis(thiazole) (7). Compound 7 was synthesized according to the same procedure for 6 to yield a yellow solid (0.71 g, 60%). ¹H NMR (400 MHz, CDCl₃): δ 8.87 (2H, s). ¹³C NMR (100 MHz, CDCl₃): δ 156.59, 152.73, 122.66. GC-MS calculated for [C₆H₂N₂S₂Se] 245.88; found 245.90.

2,6-Dibromothieno[2,3-d:5,4-d']bis(thiazole) (8). To a solution of compound 6 (0.263 g, 1.33 mmol) in dry DMF (30 mL) was added NBS (1.20 g, 6.60 mmol) in one portion. The reaction mixture was stirred at 65 °C for 4 h. It was cooled to RT, water was then added, and the reaction mixture was extracted with chloroform (3 × 50 mL). The combined organic layers were washed with brine and water, dried over MgSO₄, and filtered, and the solvent was removed *in vacuo*. Recrystallization of the crude product from methanol afforded a compound 8 as a yellow solid (0.26 g, 56%). ¹³C NMR (100 MHz, CDCl₃): δ 153.9, 135.8, 123.9. GC-MS calculated for [C₆N₂S₃Br₂] 353.75; found 353.70.

2,6-Dibromoselenopheno[2,3-d:5,4-d']bis(thiazole) (9). The same procedure as 8 was followed to synthesize compound 9. The crude product was recrystallized from a mixture of chloroform and methanol to afford a yellow solid 9 (0.38 g, 52%). ¹³C NMR (100 MHz, CDCl₃): δ 153.5, 135.2, 125.3. GC-MS calculated for [C₆N₂S₂SeBr₂] 401.70; found 401.70.

General Synthetic Procedure of P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) by Stille Cross-Coupling Reaction. In a microwave vial, equimolar amounts of the dibromo derivative 8 (0.16 mmol) and the appropriate DPP-based monomer 10 (0.16 mmol) were dissolved in anhydrous chlorobenzene (2 mL) followed by addition of tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (2 mol %, 1.85 mg) and tri(*o*-tolyl)phosphine (4 mol %, 1.95 mg). The resultant mixture was degassed for 15 min under argon and securely sealed. The polymerization was performed at 180 °C for 30 min in a microwave reactor. The reaction mixture was precipitated into a mixture of methanol (100 mL) and concentrated hydrochloric acid (2 mL) and stirred for 1 h at room temperature. The polymeric precipitate was then filtered into a cellulose thimble and was purified by Soxhlet extraction with methanol (24 h), acetone (24 h), and hexane (24 h) sequentially. The remaining polymer was dissolved in chloroform and precipitated into methanol, filtered, and dried under vacuum to afford the desired blue polymer.

P(DPPBT-BTz-S), P(DPPTT-BTz-S), P(DPPBT-BTz-Se), and P(DPPTT-BTz-Se) were synthesized according to the general procedure using the respective monomers. The data for each polymer are as follows:

P(DPPBT-BTz-S) (97 mg, chloroform fraction, 51%). GPC: M_w : 36.5 kDa; ϑ : 5.4. UV–vis: λ_{max} (dilute chloroform solution) 425, 654 nm; λ_{max} (film): 465, 656 nm.

P(DPPTT-BTz-S) (109 mg, chloroform fraction, 58%). GPC: M_{w} : 31.8 kDa; \mathcal{D} : 4.1. UV-vis: λ_{max} (dilute chloroform solution) 426, 621 nm; λ_{max} (film): 430, 628 nm.

P(DPPBT-BTz-Se) (99 mg, chloroform, fraction, 48%). GPC: M_{w} : 28.2 kDa; \mathcal{D} : 4.2. UV-vis: λ_{max} (dilute chloroform solution) 441, 683 nm; λ_{max} (film): 474, 686 nm.

P(DPPTT-BTz-Se) (89 mg, chloroform, fraction, 45%). GPC: M_w : 41.4 kDa; \mathcal{D} : 3.9. UV-vis: λ_{max} (dilute chloroform solution) 413, 630 nm; λ_{max} (film): 435, 639 nm.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.8b00826.

Experimental details, characterizations, and NMR spectra (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: mohammed.al-hashimi@qatar.tamu.edu (M.A.-H.).

ORCID [©]

Dhananjaya Patra: 0000-0002-2471-5057 Jongbok Lee: 0000-0002-0086-0938 Lei Fang: 0000-0003-4757-5664

Martin Heeney: 0000-0001-6879-5020

Mohammed Al-Hashimi: 0000-0001-6015-2178

Notes

The authors declare no competing financial interest.

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