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**Molecular Engineering of Non-Halogenated Solution-Processable Bithiazole based Electron
Transport Polymeric Semiconductors**

Boyi Fu,¹ Cheng-Yin Wang,² Bradley D. Rose,³ Yundi Jiang,¹ Mincheol Chang,¹ Ping-Hsun
Chu,¹ Zhibo Yuan,⁴ Canek Fuentes-Hernandez,² Bernard Kippelen,² Jean-Luc Brédas,³ David M.
Collard,⁴ and Elsa Reichmanis^{1,4,5*}

¹School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst
Drive, Atlanta, GA 30332-0100, U.S.A

²School of Electrical and Computer Engineering, Georgia Institute of Technology, 777 Atlantic
Dr NW, Atlanta, GA 30332-0250, U.S.A

³Solar and Photovoltaics Engineering Research Center, King Abdullah University of Science and
Technology, Thuwal 23955-6900, Kingdom of Saudi Arabia

⁴School of Chemistry & Biochemistry, Georgia Institute of Technology, 901 Atlantic Drive,
Atlanta, GA 30332-0400, U.S.A

⁵School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive,
Atlanta, GA 30332-0245, U.S.A.

* Corresponding author: ereichmanis@chbe.gatech.edu

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Abstract:

The electron deficiency and *trans* planar conformation of bithiazole is potentially beneficial for the electron transport performance of organic semiconductors. However, the incorporation of bithiazole into polymers through a facile synthetic strategy remains a challenge. Herein, 2,2'-bithiazole was synthesized in one step and copolymerized with dithienyldiketopyrrolopyrrole to afford poly(dithienyldiketopyrrolopyrrole-bithiazole), **PDBTz**. **PDBTz** exhibited electron mobility reaching $0.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in organic field-effect transistor (OFET) configuration; this contrasts with a recently discussed isoelectronic conjugated polymer comprising an electron rich bithiophene and dithienyldiketopyrrolopyrrole, which displays merely hole transport characteristics. This inversion of charge carrier transport characteristics confirms the significant potential for bithiazole in the development of electron transport semiconducting materials. Branched 5-decylheptacyl side chains were incorporated into **PDBTz** to enhance polymer solubility, particularly in non-halogenated, more environmentally compatible solvents. **PDBTz** cast from a range of non-halogenated solvents exhibited film morphologies and field-effect electron mobility similar to those cast from halogenated solvents.

1. Introduction

The development of high efficiency, air stable electron transport polymeric semiconductors for organic electronic devices has attracted much attention due to their importance in the fabrication of organic p-n junction devices, such as complementary-metal-oxide-semiconductor (CMOS)-like logic circuits,^[1-2] thermoelectrics,^[3] hetero-junction photovoltaics,^[4-6] and organic light-emitting diodes.^[7-8] For example, a combination of hole transport and electron transport semiconductors with comparable mobility values is required to implement CMOS-like logic,

which is widely used in digital integrated circuits including microprocessors, microcontrollers, and static random access memory devices.^[1, 9-10] Significant advances in the development of hole transport polymeric semiconductors have led to materials that demonstrate field-effect hole mobilities of up to $20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.^[11-12] However, less progress has been made towards the development of electron transport counterparts.^[13-16] The more limited advances in this instance result from challenges associated with the stabilization and delocalization of the lowest unoccupied molecular orbital (LUMO) of π -conjugated polymers.^[7, 13, 17-18] Stabilization of the LUMO means raising the electron affinity, which can be realized by materials that consist of electron-deficient conjugated repeat units.^[13, 18-20] The LUMO delocalization can be enhanced by backbone planarization and inter-chain stacking.^[21]

The 2,2'-bithiazole unit exhibits a number of features that could be attractive in the search for electron transport conjugated polymers. The presence of electronegative nitrogen atoms lowers the LUMO energy in comparison to analogs that consist of electron rich units such as thienyl derivatives.^[22-26] The *trans* conformation of bithiazole (with a dihedral angle between the thiazole rings close to 180° , as confirmed by density functional theory, DFT, in this study, *vide infra*) can promote polymer backbone planarity, which extends intrachain π -conjugation and interchain π - π stacking, in comparison to analogs such as biphenyl that is not coplanar.^[27-29] Thiazole has a large dipole moment of 1.6 D,^[30-31] an antiparallel alignment between the two thiazole moieties within bithiazole leads to a net zero dipole, which is one driving force for planarization of bithiazole. Additionally, the large dipole of the thiazole unit could impart strong dipole-dipole interactions between bithiazole-based polymer chains.^[32]

The bithiazole unit has been primarily used to build hole transport donor-acceptor π -conjugated copolymers; bithiazole was considered as a weak acceptor. Recent studies indicated

the feasibility of using bithiazole in developing electron transport small molecular semiconductors;^[32-33] and in few cases, bithiazole-based polymers were exhibited ambipolar properties.^[34] Hence, the development of electron transport polymeric semiconductors based on bithiazole could be envisioned, though no study has been reported as yet. One significant challenge lies in the development of an efficient synthetic pathway to incorporate bithiazole units into π -conjugated molecules and polymers.^[24, 32] Herein 2,2'-bithiazole was synthesized in one step, and copolymerized with a second electron deficient monomer, dithienyl diketopyrrolopyrrole (TDPP), to afford the first example of a bithiazole based electron transport polymer, poly(dithienyldiketopyrrolopyrrole-bithiazole), **PDBTz**, as shown in **Scheme 1**. An isoelectronic conjugated polymer consisting of alternating electron rich 2,2'-bithiophene units and TDPP (PDQT, see structure shown in **Figure 1**) exhibits pure hole transport behavior.^[35-37] Through comparison of **PDBTz** with PDQT, we set out to explore the capability of bithiazole on tailoring hole and electron transport characteristics, with the expectation that the bithiazole analog would enhance electron transport behavior.

Side chain substitution on the bithiazole and dithienyl groups was avoided to minimize steric effects within the **PDBTz** backbone. Branched 5-decylheptadecyl (5-DH) side chains were utilized as they had been shown in our previous study to facilitate both polymer solubility and effective π - π inter-chain interactions by virtue of having a branch point remote from the polymeric main chain.^[38] Such a side chain was incorporated into the TDPP unit to promote π - π inter-chain interactions and solubility in a wide range of solvents including non-halogenated options such as xylenes or 1,2,3,4-tetrahydronaphthalene (THN), which are more eco-friendly than halogenated alternatives.

Current semiconducting polymer solution-processes for organic electronic devices primarily depend on the use of halogenated solvents such as chlorobenzene, *o*-dichlorobenzene (DCB), or 1,2,4-trichlorobenzene (TCB), which present significant health and environmental challenges and severely limit their future application. Thus, materials that can be processed from non-halogenated media are highly desirable.^[39-42] However, few such examples have been reported, and electron transport polymeric semiconductors processable from non-halogenated solvents are especially rare.^[9] Here, **PDBTz** thin-film OFETs fabricated using non-halogenated *o*-xylene, *p*-xylene, and THN, as well as DCB were investigated. This allowed for a systematic study of solvent on semiconducting polymer thin-film ordering, texture, charge carrier transport performance, and the practicality of developing high mobility n-channel OFET devices via more environmentally-benign processing.

2. Results

2.1. Polymer Synthesis, Solubility, and Thermal Properties

The synthesis of **PDBTz** is outlined in **Scheme 1**, and complete synthetic details are provided in the Supporting Information (**S.I.**). Commercially available 2-bromothiazole was homocoupled to afford 2,2'-bithiazole, **1**.^[43] Metallation of **1** afforded distannane monomer **2**.^[25] Conversion of **1** to **2** approached 100 % based on ¹H NMR analysis. However, **2** has limited stability: demetallation of 25-30 mol% of **2** back to **1** takes place within one week (**Figure S6, S.I.**). Hence, the polymerization should be carried out with freshly prepared monomer. **PDBTz** was prepared by Stille step-growth polymerization of monomer **2** with 3,6-bis(5-bromo-2-thienyl)-*N,N*-di(5-decylheptadecyl)diketopyrrolopyrrole monomer (**3**)^[38] under microwave irradiation (160 °C for 2 h). The crude polymer was purified through precipitation from methanol followed by Soxhlet

extraction to afford **PDBTz** that was further characterized. Gel permeation chromatography (GPC; 135 °C with TCB as eluent) indicated a number-average molecular weight (M_n) of 64 kg mol⁻¹, which corresponds to a degree of polymerization (DP) of 53, as shown in **Table 2**. The relatively large PDI of 3.6 is likely due to the polymer aggregation in solution.

The attainment of relatively high molecular weight material suggested that the resulting polymer has good solubility in *o*-xylene. Process solvents have a significant influence on the molecular ordering, morphology, and charge carrier mobility of thin-film polymeric semiconductors. Hence, the characterization and processing of **PDBTz** in *o*-xylene along with two other similar non-halogenated solvents, *p*-xylene and THN, were explored. The theoretical solubility of **PDBTz** was estimated using the Hansen solubility parameter space (R_a),^[39, 44] which describes the difference in Hansen solubility parameters (HSPs) of **PDBTz** (1) and solvents (2), as shown in **Equation 1**:

$$R_a = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2} \quad \text{Equation 1}$$

where δ_d , δ_p , and δ_h refer to the dispersion force solubility parameter, dipolar intermolecular force solubility parameter, and hydrogen bonding solubility parameter, respectively. Lower values of R_a predict a lower cohesive energy density difference between **PDBTz** and a solvent, which corresponds to a weaker thermodynamic driving force for phase separation of solute from solvent and a higher solubility of the polymer.^[45] The pertinent physical properties of **PDBTz** and the four solvents (DCB, *o*-xylene, *p*-xylene, and THN) are listed in **Table 1** (the experimental and calculation details are provided in the **S.I.**). Solutions of **PDBTz** in the two xylenes exhibit similar R_a values as for **PDBTz** in DCB, whereas the corresponding value for THN is much lower. These results suggest similar or even better **PDBTz** solubility in the non-halogenated solvents than in DCB. Experimental results indicate that **PDBTz** possesses

solubility in the range of 5-9 mg mL⁻¹ in the four solvents at 90 °C. **PDBTz** exhibits the lowest solubility in *p*-xylene (5 mg mL⁻¹), while the solubility is highest with THN (9 mg mL⁻¹).

PDBTz is stable up to 417 °C (see TGA characterization, **Table 2** and **Figure S7**), indicating high thermal stability. The polymer exhibits one endothermic ($T_h = -44$ °C) and one exothermic transition ($T_c = -47$ °C) upon heating and cooling, respectively (see DSC characterization, **Table 2** and **Figure S7**). In light of prior results using the same substituent, this most likely corresponds to the disordering and reordering processes associated with the 5-DH side chains.^[38]

2.2. Photophysical Properties

The spectroscopic features of **PDBTz** solutions in the different solvents are quite similar. Peaks are observed at ca. 325, 446, 702, and 767 nm in the spectra of **PDBTz** in each solvent, as shown in **Figure 2a**. The bands with λ_{max} at ca. 446, 702, and 767 nm may be ascribed to TDPP units since solutions of the analogous diketopyrrolopyrrole-*oligo*thiophene polymers exhibit similar features;^[11, 35-37] while the **PDBTz** band at λ_{max} of 325 nm was assigned to the bithiazole units, given that 2,2'-bithiazole (compound **1**) in THF exhibits an absorption band with λ_{max} at 320 nm (**Figure 2a**). The absorption spectra of **PDBTz** thin-films (**Figure 2b**) are essentially identical to those of the solution spectra, suggesting a similar rigid polymer chain conformation in the solid state as in solution. These results also suggest the self-assembly of **PDBTz** polymer chains in solution. Taking account of low **PDBTz** concentration in solution (10⁻⁶ M in **Figure 2a**), **PDBTz** has strong inter-chain interactions. Based on the absorption onset, the optical band gap (E_g^{opt}) of **PDBTz** is estimated as 1.33 eV. The increase in the intensity of the peak at 697 nm relative to that at 765 nm for the film (**Figure 2b**) in comparison to the solution (**Figure 2a**) suggests that **PDBTz** favors the interchain excitonic coupling^[46-47] in thin films. **PDBTz** films

cast from solutions in DCB, *o*-xylene, *p*-xylene, and THN exhibit similar spectroscopic characteristics, which indicates similar thin-film microstructure (ordering and orientation) for all of the systems, although the film prepared using *p*-xylene is likely to form a stronger interchain excitonic coupling.

2.3. Characterization of Electronic Structure

The redox potentials of **PDBTz** thin-films were investigated using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) (**Figure S9**). **PDBTz** exhibits an onset for reduction at -1.30 V versus Fc/Fc⁺ (-5.08 eV versus vacuum^[48-49]) by CV, and -1.18 V (versus Fc/Fc⁺) by DPV, as shown in Table 3, which corresponds to an electron affinity of -3.8 to -3.9 eV. The reversibility of the reduction, as shown in **Figure 2c**, demonstrates the stability of reduced **PDBTz** as an electron carrier. However, **PDBTz** exhibits an irreversible electrochemical oxidation process as demonstrated by both CV and DPV, with a peak onset at +0.82 V (versus Fc/Fc⁺) by CV and +0.66 V (versus Fc/Fc⁺) by DPV (**Figure S9b**). These electrochemical results are opposed to the typical hole transport polymeric semiconductors that have a reversible oxidation while no obvious reduction.^[20, 35, 38]

Thin films of **PDBTz** were characterized by ultraviolet photoelectron spectroscopy (UPS) to determine the intrinsic ionization potential (IP) and work function (ϕ) (**Table 3, Figure S10**). The 5.54 eV **PDBTz** ionization potential suggests good ambient stability towards oxidation.^[18] Taking into account an optical gap of *ca.* 1.33 eV and an exciton binding energy in the range of 0.3-0.5 eV,^[50] would lead to an electron affinity on the order of -3.7 to -3.9 eV, which is consistent with the CV/DPV estimate. Such an electron affinity implies a good ambient stability for electron transport organic semiconductors.^[7, 13]

2.4. Field-effect electron transport

PDBTz charge carrier transport properties were studied using organic field-effect transistors (OFETs) with top-contact/bottom-gate (TCBG) and bottom-contact/top-gate (BCTG) architectures, as shown in **Figure 3**. With the aim of minimizing barriers to electron injection, and taking into account the electron affinity of **PDBTz** (in the range of -3.8 to -3.9 eV), calcium (work function, $\phi = 2.9$ eV)^[51] and ethoxylated polyethylenimine (PEIE) doped silver ($\phi = 3.7$ eV)^[52] were selected as source and drain electrodes in TCBG and BCTG devices, respectively (**Figure 2d**). TCBG and BCTG OFETs were initially fabricated based on spin-coated **PDBTz**/DCB solutions (5 mg mL⁻¹). The results are listed in **Table 4**. TCBG OFETs making use divinyltetramethylsiloxane-bis(benzocyclobutene) (BCB)^[17, 51] as the dielectric layer to minimize electron traps exhibited ideal n-channel I-V transfer characteristics, with average and maximum electron field-effect mobility values (μ_e) of 0.17 and 0.26 cm²V⁻¹s⁻¹, respectively, and a current on/off ratio ($I_{ON/OFF}$) greater than 10⁵. Comparable electron transport performance was determined for **PDBTz**-based BCTG OFETs with CYTOP/Al₂O₃ as dielectric and encapsulation bilayers. BCTG devices were characterized based on a 10 V source-drain voltage (V_{SD}) and a gate voltage (V_G) in a range of 0 to 16 V, revealing the feasibility of using **PDBTz** for high performance devices under relatively low operating voltages. Notably, the **PDBTz** devices exhibited similar performance to those prepared with poly(NDI2OD-T2) (0.1 cm²V⁻¹s⁻¹), a benchmark electron transport polymeric semiconductor, based on our previous study.^[52] Both **PDBTz** device architectures exhibited excellent n-channel transistor behavior with low (4-8 V) threshold voltages (V_{th}) and negligible hysteresis (**Figure 3b,f**). The device performance was determined after thermal annealing at 150 °C. To explore **PDBTz** air stability, devices encapsulated by a CYTOP layer (**S.I.**) were stored at 25 °C and 55-70 % RH, and were

characterized periodically over 4 months. No appreciable changes were observed in $I_{\text{ON/OFF}}$ and only a small decrease in μ_e was observed over this period (**Figure 3d,h**). The ambient stability correlates with the low polymer frontier energy levels. Further enhancement of device stability against O_2 and H_2O is expected through inorganic/organic multilayer encapsulation.^[53]

PDBTz possesses similar solubility in non-halogenated *o*-xylene, *p*-xylene, and THN, as in DCB (*vide supra*). **PDBTz** OFET devices were also fabricated by spin-coating polymer solutions in *o*-xylene (5 mg mL⁻¹), *p*-xylene (4 mg mL⁻¹) and THN (5 mg mL⁻¹) to evaluate the impact of solution-processing from non-halogenated vs. halogenated solvents. As shown in **Table 4**, **PDBTz** electron transport performance in BGTC devices was comparable in devices fabricated from all four solvents, with an average μ_e of 0.18 cm²V⁻¹s⁻¹. A maximum value of μ_e (0.3 cm²V⁻¹s⁻¹) was obtained in devices prepared from THN and *p*-xylene. **PDBTz** based BCTG transistors fabricated from solutions in xylenes and THN exhibited μ_e (0.08 cm²V⁻¹s⁻¹) relatively lower but close to that found for DCB (0.15 cm²V⁻¹s⁻¹, in **Table 4**).

2.5. Thin film morphology and microstructure

The surface morphologies of **PDBTz** films that were prepared by spin-casting from the four solutions onto BCB modified Si substrates were characterized using tapping-mode atomic force microscopy (AFM). All of the films exhibited similar nanostructured morphologies with similar grain sizes of 30-60 nm and surface roughness of 1.04-1.38 nm, as shown in **Figure 4**. This suggests comparable contact between spin-coated films and the source-drain electrodes of TCBG OFETs.

The polymer films were investigated further by two-dimensional grazing incidence wide angle X-ray scattering (2D-GIWAXS) to explore the relationship between film microstructure and electron transport performance. Films were prepared from drop-cast **PDBTz** solutions in DCB, *o*-xylene, *p*-xylene, and THN onto Si substrates (300 nm SiO₂ dielectric on heavily p-doped Si) that had been functionalized with cross-linked BCB. X-ray scattering patterns, before and after thermal annealing at 150°C, were similar for each sample, regardless of solvent, as shown in **Figure 5**. All of the films exhibited well-defined $\langle h00 \rangle$ diffraction patterns along the q_z (out-of-plane) axis that is attributed to a highly ordered lamellar d -spacing structure between polymer chains that are segregated by 5-DH chains. In addition the films exhibited $\langle 010 \rangle$ peaks along the q_{xy} (in-plane) axis arising from π - π stacking of **PDBTz** backbones. The spacing distances (**Figure 6a, e**), full-width-at-half-maximum (FWHM, **Figure 6b, f**), coherence length (mean size of ordered crystalline domains, **Figure 6c, g**), and relative degrees of crystallinity^[15] (rDoC, **Figure 6d**) indicated by the $\langle 100 \rangle$ and $\langle 010 \rangle$ peaks are similar for **PDBTz** films from all four solutions both before and after annealing. In light of the length of a heptadecyl chain in an all-trans conformation (*ca.* 17.5 Å), the **PDBTz** lamellar d -spacing (24-25 Å) suggests that the side chains are interdigitated within the crystalline lattice.

The **PDBTz** $\langle 100 \rangle$ and $\langle 010 \rangle$ patterns exhibit highly anisotropic distributions along with the azimuthal angle, χ , as seen in **Figure 5**. This was quantitatively evaluated by Herman's orientation function (S , the calculation details are provided in **S.I.**)^[54] Results of this analysis are shown in **Table 5**. The four **PDBTz** films exhibited essentially identical S values that approached 0.9 for the $\langle 100 \rangle$ diffraction, which is regarded as a high value for a polymer system and is indicative of a high degree of alignment parallel to χ_{max} ; on the other hand, χ_{max} for $\langle 100 \rangle$ is close to zero. These results quantitatively demonstrate that all four **PDBTz** films have average

lattice planes oriented normal to the q_{xy} axis, which corresponds to an edge-on orientation, as shown in **Scheme S1**. The $\Delta\chi_{\text{FWMH}}$ term refers to the full width at half maximum of peak intensity along the χ axis. All four films display a value of $\Delta\chi_{\text{FWMH}}$ in a range of 9 to 13° for the $\langle 100 \rangle$ diffraction. Such a narrow distribution further confirms a high degree of orientation along χ_{max} . A similar phenomenon is observed for the $\langle 010 \rangle$ pattern: the four samples have an S value of approximately 0.8 at $\chi_{\text{max}} \approx 86^\circ$. These results are also consistent with a highly aligned edge-on orientation for the average lattice planes, which mirrors the $\langle 100 \rangle$ analysis. In summary, all four **PDBTz** films exhibit a highly edge-on aligned orientation irrespective of casting solvents.

The FWHM values for the $\langle 200 \rangle$ and $\langle 300 \rangle$ diffractions relative to that of the $\langle 100 \rangle$ diffraction (i.e., $\text{FWHM}_{\langle 200 \rangle} / \text{FWHM}_{\langle 100 \rangle}$ and $\text{FWHM}_{\langle 300 \rangle} / \text{FWHM}_{\langle 100 \rangle}$) underwent no obvious change upon annealing (**Figure 6h**), which demonstrates identical enhancement in the lattice cumulative order.^[55] After annealing, all **PDBTz** films exhibited a reduction in FWHM and corresponding improvement in coherence length for both $\langle 100 \rangle$ and $\langle 010 \rangle$ patterns (**Figure 6b, f and c, g**), together with a 3-10% increase in rDoC, which correlate well with the observed increase in electron mobility upon annealing. In consideration of the subtle increase in orientation distribution within all four **PDBTz** films after thermal annealing, as shown by changes in S and $\Delta\chi_{\text{FWMH}}$ (**Table 5**), annealing primarily impacts **PDBTz** ordering and grain size, while crystallite growth likely proceeds equally along each orientation distribution direction. The microstructure and morphology analyses demonstrate that the processing solvents have similar effect on the morphology, molecular ordering, orientation, and rDoC of **PDBTz** films, in good accord with very similar electron transport properties for the respective samples.

2.6. Comparison of **PDBTz** with PDQT

Several groups have reported the copolymerization of bithiophene-containing monomers and TDPP to afford poly(diketopyrrolopyrrole-quaterthiophene), PDQT,^[35-37] whose chemical structure is shown in **Figure 1d**. Electrochemical studies of PDQT reveal reversible oxidation, and hole transport properties are observed in OFETs prepared from this material. In contrast, **PDBTz**, where the bithiophene segment of each PDQT repeat unit is replaced by bithiazole, displays reversible electrochemical reduction and electron transport behavior. This shift from hole transport for PDQT to electron transport for **PDBTz** clearly demonstrates a significant impact for bithiazole to instill electron transport characteristics.

For a side-by-side comparison of these two polymers, **PDBTz** was applied to BCBG transistors with Au ($\phi = 5.1 - 5.5$ eV) as source-drain electrodes, which have the same electrode-injection condition to PDQT based device. The results exhibited a $0.2\text{-}0.3\text{ cm}^2/\text{V}^{-1}\text{s}^{-1}$ of μ_e similar to those shown in TCBG and BCTG transistor configurations. A weak hole mobility (μ_h , on the order of $10^{-3}\text{ cm}^2/\text{V}^{-1}\text{s}^{-1}$) was observed due to the close ϕ of Au to HOMO of **PDBTz**. This much greater μ_e than μ_h suggests that the bithiazole-based counterpart favors electron transport.

Density functional theory (DFT) calculations using tuned- ω B97X/cc-pVDZ were utilized to first explore the torsional potentials of **PDBTz** and PDQT subunits; the results were compared to reference single-point SCS-MP2 calculations (**Figure 1a**, see **S.I.** for details).^[56-58] Tuned- ω B97X calculations were also carried out for the monomer through tetramer of **PDBTz** and PDQT. The calculations indicate that within one **PDBTz** repeat unit, the bithiazole segment adopts a *trans* coplanar conformation with a dihedral angle (ϕ) of 180° between the two thiazole rings (**Figure 1a**). This contrasts with the bithiophene moiety within one PDQT repeat unit, in which the two rings are twisted at an angle of 155° (**Figure 1a**). Expectedly, replacing

bithiophene with bithiazole stabilizes both the LUMO and HOMO levels of **PDBTz** by about 0.2-0.3 eV compared to PDQT (**Figure 1b**). Interestingly, as shown in **Figure 1c**, both the LUMO and HOMO wavefunctions are delocalized along the **PDBTz** backbone.

3. Conclusion

An electron transport polymeric semiconductor, **PDBTz**, was prepared upon copolymerization of the electron deficient bithiazole with dithienyldiketopyrrolopyrrole. **PDBTz** has a low optical bandgap (1.33 eV) and high electron affinity (-3.7 – -3.9 eV). **PDBTz** based thin-film OFETs exhibited an electron mobility reaching $0.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with $I_{\text{ON/OFF}}$ greater than 10^5 . No substantial performance changes were observed in $I_{\text{ON/OFF}}$ and a small decrease in μ_e was noted upon storing **PDBTz** OFETs encapsulated by CYTOP at 25 °C and 55-70 % RH over 4 months. Incorporation of 5-DH side chains instilled **PDBTz** with good solubility in non-halogenated xylenes and THN, in comparison to halogenated DCB. **PDBTz** films cast from these four solvents displayed similar morphologies (ordering and texture) and field-effect electron mobility. The results demonstrate the feasibility for developing high performance electron transport materials that are compatible with more environmentally benign process options. DFT calculations demonstrated that the incorporation of bithiazole induces a more planar geometry and lowers both the LUMO and HOMO energy levels compared to bithiophene, a typical electron rich building block used to develop electron transporting polymeric semiconductors.

Many current electron transport and ambipolar polymeric semiconductors are based upon copolymerization of bithiophene with electron acceptors, such as naphthalenedicarboximide, perylenedicarboximide, or isoindigo derivatives.^[9, 16, 59-61] In this study, bithiazole has been

shown as a promising building block for the next generation of electron transport polymeric semiconductors with enhanced mobility and stability.

Supporting Information

The synthetic details of preparing monomers and polymers, characterization methods, OFET fabrications, computational details, **Scheme S1-2**, **Table S1** and **Figure S1 – S11** are included in the Supporting Information, which is available from the Wiley Online Library or from the corresponding author.

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Scheme 1. The synthetic route to prepare **PDBTz**. The inserted image (bottom right) shows a **PDBTz** solution in *o*-dichlorobenzene (DCB) and a spin-coated film of **PDBTz** from DCB (5 mg mL⁻¹) on a glass substrate.

Figure 1. (a) DFT (tuned- ω B97X) and SCS-MP2 torsional energies of **PDBTz** subunits at different dihedral angles; dihedral angles (φ) for the subunits are highlighted in blue. (b) DFT HOMOs and LUMOs of the monomer ($n=1$), dimer ($n=2$), trimer ($n=3$), and tetramer ($n=4$) of **PDBTz** and PDQT. Illustrations of the DFT frontier molecular orbitals for the dimers of (c) **PDBTz** and (d) PDQT.

Figure 2. The photophysical and electrochemical properties of **PDBTz**: (a) UV/vis absorption spectra of **PDBTz** in solution (10^{-6} M; DCB: *o*-dichlorobenzene, OX: *o*-xylene, PX: *p*-xylene, THN: tetrahydronaphthalene, CHCl_3 : chloroform, CB: chlorobenzene, TCB: 1,2,4-trichlorobenzene); (b) UV/vis absorption spectra of **PDBTz** thin-films; (c) cyclic voltammograms of a drop-cast film of **PDBTz** on a platinum electrode (in 0.5 M Bu_4NPF_6 /acetonitrile) at scan rates between 20 mV s^{-1} and 200 mV s^{-1} (five cycles at each scan rate); (d) Ionization potential (IP) and electron affinity (EA) of **PDBTz** and workfunctions of Ca and PEIE doped Ag.

Figure 3. I-V curves for PDBTz-based OFETs with bottom-gate/top-contact (a) and top-gate/bottom-contact (e) architectures, and their corresponding transfer (b and f) and output (c and g) plots; effect of OFET stability under ambient conditions (25 °C and 55-60 %RH) on electron mobility (d) and $I_{ON/OFF}$ (h).

Figure 4. Tapping mode AFM height (top row) and phase (bottom row) images of **PDBTz** recorded after annealing each film at 150 °C for 30 min followed by rapid cooling to room temperature.

Figure 5. 2D-GIWAXS area detector images of **PDBTz** films cast from DCB (a, b); *o*-xylene (c, d); *p*-xylene (e, f); and THN (g, h) solutions, respectively. Top row, as-spun films; bottom row, samples after annealing at 150 °C for 30 min followed by rapid cooling to room temperature.

Figure 6. *d*-spacing (a and e), FWHM (b and f), and coherence length (c and g) for **PDBTz** cast from DCB, *o*-xylene (OX), *p*-xylene (PX), and tetrahydronaphthalene (THN) solutions, respectively, along the <100> and <010> peaks. The relative degree of crystallinity (rDoC, d). Hollow bars: as cast films; black bars: films after 150 °C/30 min anneal. (h) Relative FWHMs of <200> and <300> to those of <100>: $\text{FWHM}_{\langle 200 \rangle} / \text{FWHM}_{\langle 100 \rangle}$ and $\text{FWHM}_{\langle 300 \rangle} / \text{FWHM}_{\langle 100 \rangle}$ for as cast films (bars with no oblique line) and films after thermal annealing at 150 °C for 30 min (bars with oblique lines).

Table 1. Hansen solubility parameters (δ_d , δ_p , and δ_h) and boiling points (b.p.) for **PDBTz**, dichlorobenzene (DCB), *o*-xylene, *p*-xylene and tetrahydronaphthalene (THN); and Hansen solubility parameter spaces (R_a) and solubilities of **PDBTz** in each solvent.

	δ_d^a	δ_p^b	δ_h^c	R_a^d	Solubility ^e	b.p.
	[MPa ^{1/2}]	[MPa ^{1/2}]	[MPa ^{1/2}]	[MPa ^{1/2}]	[mg mL ⁻¹]	[°C]
PDBTz	20.0	1.2	5.1			n/a
DCB	19.2	6.3	3.3	5.64	7	180
<i>o</i> -Xylene	17.8	1.0	3.1	4.84	7	144
<i>p</i> -Xylene	17.6	1.0	3.1	5.20	5	138
THN	19.6	2.0	2.9	2.47	9	207

^a) δ_d : dispersion force solubility; ^b) δ_p : dipolar intermolecular force solubility; ^c) δ_h : hydrogen bonding solubility; ^d) R_a : (HSP difference between PDBTz and solvents) calculated by Equation 1; ^e): PDBTz solubility in solvent at 90 °C.

Table 2. PDBTz molecular weight, photophysical, and thermal properties

Polymer	Mn	PDI	DP	Absorption maximum [eV]		E_g^{opt}	T_d^a	T_h^b	T_c^c
	[kDa]			Solution	Film	[eV]	[°C]	[°C]	[°C]
PDBTz	64	3.6	53	1.62, 1.77, 2.78, 3.82	1.62, 1.78, 2.77, 3.80	1.33	417	-44	-47

^a) T_d : decomposition temperature, defined as the temperature in which the polymer undergoes 5 wt% weight loss; ^b) T_h : phase transition temperature upon heating process; ^c) T_c : phase transition temperature upon cooling process.

Table 3. PDBTz ionization potential and electron affinity.

Polymer	UPS			DPV		CV	
	IP ^{a)} [eV]	ϕ [eV]	EA ^{b)} [eV]	E_{red} ^{c)} [V]	EA [eV]	E_{red} ^{c)} [V]	EA [eV]
PDBTz	5.54	4.90	-3.7 - -3.9	-1.18	-3.90 ^{d)}	-1.30	-3.75 ^{d)}

^{a)} IP: ionization potential; ^{b)} EA: electron affinity, taking into account an optical gap of *ca.* 1.33 eV and an exciton binding energy in the range of 0.3-0.5 eV; ^{c)} E_{red} : reduction potential; ^{d)} calculated from onsets for reduction versus Fc/Fc+ (-5.08 eV versus vacuum^[48-49]) + 5.08 eV.

Table 4. Electron transport properties of PDBTz fabricated on top-contact/bottom-gate and bottom-contact/top-gate OFETs ^{a)}

Solvent	TCBG				BCTG			
	$\mu_{\text{e,FET}}$ [cm ² V ⁻¹ s ⁻¹]		$I_{\text{ON/OFF}}$	V_{th}	$\mu_{\text{e,FET}}$ [cm ² V ⁻¹ s ⁻¹]		$I_{\text{ON/OFF}}$	V_{th}
	avg.	max			avg	max		
DCB	0.17 (±0.05)	0.26	10 ⁵	5.5 (±1.2)	0.17 (±0.04)	0.21	10 ⁵	7.8 (±0.4)
<i>o</i> -Xylene	0.14 (±0.04)	0.18	10 ⁵	8.0 (±1.2)	0.08	0.08	10 ⁴	0.8
<i>p</i> -Xylene	0.24 (±0.06)	0.31	10 ⁵	4.0 (±1.0)	0.08 (±0.002)	0.08	10 ³	0.8 (±0.3)
THN	0.18 (±0.07)	0.30	10 ⁵	6.0 (±3.5)	0.09 (±0.007)	0.11	10 ³	0.1 (±0.1)

^{a)} BGTC characterization results were based on 5–8 of devices for each fabrication conduction; TGBC characterization results were 3 – 6 of devices for each fabrication conduction. These OFET devices were thermally annealed at 150 °C for 30 min.

Table 5. Hermans' orientation function of <100> and <010> peaks in **PDBTz** films cast from DCB, *o*-xylene, *p*-xylene and THN, before and after annealing

Solvent	RT ^{a)}						150 °C ^{b)}					
	<100>			<010>			<100>			<010>		
	<i>S</i> ^{c)}	$\chi_{\max}$ ^{d)}	$\Delta\chi_{\text{FWHM}}$ ^{e)}	<i>S</i>	$\chi_{\max}$	$\Delta\chi_{\text{FWHM}}$	<i>S</i>	$\chi_{\max}$	$\Delta\chi_{\text{FWHM}}$	<i>S</i>	$\chi_{\max}$	$\Delta\chi_{\text{FWHM}}$
DCB	0.85	1.8	12.3	0.66	4.5	21.3	0.83	1.9	11.7	0.62	3.5	23.1
<i>o</i> -Xylene	0.88	1.9	9.7	0.76	3.8	19.7	0.90	1.1	7.6	0.77	4.4	19.2
<i>p</i> -Xylene	0.87	2.8	10.9	0.81	4.6	17.0	0.89	1.4	8.4	0.79	4.0	19.0
THN	0.87	2.1	10.9	0.72	4.0	23.9	0.90	1.7	9.3	0.73	4.0	19.4

^{a)} **PDBTz** films as-spun from four solutions; ^{b)} **PDBTz** films were thermally annealed at 150 °C for 30 min; ^{c)} Hermans' orientation function; ^{d)} the azimuthal angle at which X-ray scattering intensity reaches the maximum; ^{e)} absolute values of χ distribution corresponding to full width at half maximum of peak intensity.

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