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Tuning the Electronic Properties of Poly(thienothiophene vinylene)s via Alkylsulfanyl and Alkylsulfonyl Substituents

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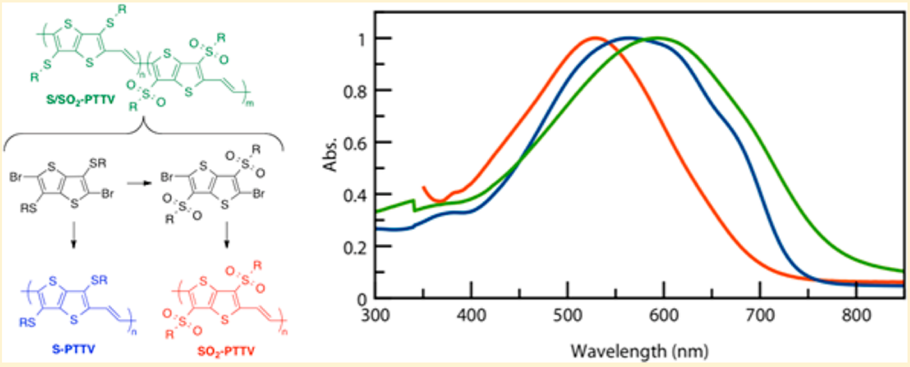
Ⓢ *Supporting Information*



ABSTRACT: The use of alkylsulfanyl and alkylsulfonyl side chains are demonstrated to be a useful synthetic strategy for tuning the electronic properties of organic semiconductors, as shown in thienothiophene vinylene polymers. By changing the oxidation state of sulfanyl to sulfonyl, we lower the HOMO and LUMO energy levels of our substituted polymers, as well as enhance their fluorescence. Fine-tuning of the energy levels was achieved by combining sulfanyl and sulfonyl substituted thienothiophene monomers through random polymerization, yielding polymers with low-band gaps (1.5 eV) yet benefiting from a structurally uniform conjugated backbone. The effects of these functional side chains are presented through DFT calculations, UV−vis, fluorescence, and electrochemical measurements, as well as crystallographic analysis of a sulfanyl-substituted oligomer. The semiconducting properties of the new polymers are studied in OFET and OPV devices.

■ INTRODUCTION

Thiophene-based conjugated polymers are important semiconducting materials with widespread applications in organic light-emitting diodes (OLEDs), field-effect transistors (OFETs), and photovoltaic solar cells (OPVs).[1] Polythiophenes are now ubiquitous in the field of organic semiconductors since they are easily functionalized and show great charge transport properties. Poly(3-hexylthiophene) (P3HT) for example, has become the benchmark donor material for bulk heterojunction solar cells, though its efficiency is limited by a relatively large band gap (E_g = 1.9 eV) and high HOMO level (−5.1 eV).[2]

Since P3HT, thiophene-based polymers have been tirelessly modified to create new high performance materials. The dominant approach is incorporating electron-deficient monomer units with electron-rich thiophene to create donor−acceptor systems that promote intrachain charge transfer, lowering the band gap of the polymer.[3] This, however, requires the synthesis of two different monomer units, complicates the structure-properties relationships and creates a polarization along the conjugation backbone. Instead of altering the backbone, a polymer's energy levels can be directly tuned through substituents, a method that is underutilized in conjugated polymer chemistry.

For example, poly(3-alkoxythiophene) showed a smaller band gap (1.60 eV) than P3HT due to increased rigidity ascribed to S···O interactions, but the electron donating effect of the alkoxy group raised the HOMO level (−4.47 eV).[4] Poly(3-cyano-4-hexylthiophene), conversely, was found to have a lower HOMO level (−6.1 eV), but a larger band gap (2.3 eV).[5] Substituents such as fluorine,[6] fluoroalkyl,[7] thienyl,[8] dicyanoethene,[9] alkoxy groups,[10] nitro groups,[11] and esters[12] have also been explored in polythiophenes.

Alkylsulfanyl substituents are of particular interest for several reasons: the van der Waals radius of sulfur (~0.18 nm) is less than that of $-CH_2$ (~0.20 nm) which slightly reduces steric strain compared to alkyl substituents;[13] they impart solubility to the polymer; and, in polythiophenes, they can act as mild

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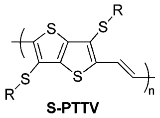
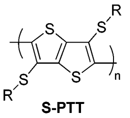
electron acceptors, lowering the HOMO levels.[14,15] Furthermore, their electron withdrawing effect can be tuned by changing the oxidation state of sulfur from sulfanyl (−SR) to sulfinyl (−SOR) or sulfonyl (−SO_2R). Sulfonyl groups have been shown to increase fluorescence in polymers[16] and oligomers.[17] They were recently employed as electron withdrawing substituents in a donor−acceptor conjugated polymer for OPVs,[18] but there exists no detailed or comparative studies of their electronic effects in semiconducting materials.

We were interested in a comparative analysis of the effect of alkylsulfanyl and alkylsulfonyl substituents on the electronic properties and behavior of conjugated polymers in semiconducting device applications. We have chosen poly(thieno[3,2-*b*]thiophene vinylene) as the conjugated backbone, taking into consideration relative structural simplicity, planarity, and a low expected band gap.

Thieno[3,2-*b*]thiophene's (TT) fused unit fosters electron delocalization by reducing the bond length alternation (compared to simple thiophene).[19] Owing to the 180° coupling geometry of TT (cf. ≈ 150° for thiophene), its polymers strongly prefer a linear rod-like structure and show increased crystallinity and charge mobilities.[20,21] A vinylene spacer reduces the twist caused by repulsions between substituents and "dilutes" the aromatic nature of the TT moieties. Both of these effects promote electron delocalization and shrink the band gap of the polymer.

In this paper we report the synthesis and spectroscopic, structural, and device characterization of poly(3,6-dialkylsulfanylthieno[3,2-*b*]thiophene vinylene), **S-PTTV**, its oxidized derivative poly(3,6-dialkylsulfonylthieno[3,2-*b*]thiophene vinylene), **SO_2-PTTV**, and the random copolymer incorporating both sulfanyl and sulfonyl units, **S/SO_2-PTTV**. Comparing their properties to models of unsubstituted **H-PTTV** and similarly substituted polymer without vinylene linker (**S-PTT**) we explore the complex effect that substituents play in these conjugated systems. Two dimers **S-2TTV** and **SO_2-2TTV** were also synthesized to understand the substituent effects in a simplified system.


S-PTTV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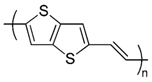
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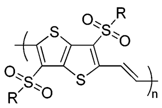
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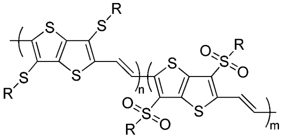

S/SO_2-PTTV

■ RESULTS AND DISCUSSION

Theoretical Calculations. Density functional theory (DFT) calculations at the B3LYP/6-31G(d) level were performed on a series of substituted TT oligomers (n = 1, 2, ..., 7) as well as for the infinite polymers, under periodic boundary conditions (PBC). The side chains were modeled with methyl groups. The HOMO, LUMO, and band gap values of the corresponding polymers, along with optimized dihedral angles are listed in Table 1. The model polymers **S-PTT**, **H-PTTV** and **P3MT** (a model of regioregular poly(3-alkylthiophene)[19]) were not experimentally studied in this paper, but are given for comparison.

Table 1. Calculated Energy Levels and Geometry of the Polymers

polymer	HOMO (eV)	LUMO (eV)	E_g (eV)	dihedral (deg)[a]
P3MT	−4.31	−2.32	1.99	0
H-PTTV	−4.53	−2.74	1.79	0
S-PTT	−5.45	−2.23	3.22	55
	−4.72	−2.79	1.93	0[b]
S-PTTV	−4.67	−2.93	1.74	1
SO_2-PTTV	−5.60	−3.76	1.84	10
S/SO_2-PTTV[c]	−5.15	−3.34	1.81	4

[a] The dihedral angle between the thiophene ring and the next conjugated unit. [b] The dihedral angle is restrained to 0°, which destabilizes the structure by 1.35 kcal/mol. [c] PBC calculations of an alternating polymer structure (AD)n. The block copolymer (AADD)n showed a 0.06 eV lower band gap: HOMO = −5.12 eV; LUMO = −3.37 eV.

As expected based on the behavior of sulfanyl-substituted oligothiophenes,[22] the alkylsulfanyl groups cause a large twist (55°) in poly(thienothiophene) **S-PTT**, disrupting the conjugation. Consequently, a very large band gap of 3.22 eV is predicted for this polymer by DFT. This is higher than the ≈2.2 eV optical band gap reported[13] for hexylsulfanyl **S-PTT** in solution (in the solid state the band gap was further lowered to 1.74 eV). These observations suggest planarization of the polymer chain (see below); indeed, calculations of a fully planarized S-PTT polymer predict a band gap of 1.93 eV. The steric repulsions of the substituents is removed by separating the TT units with a vinylene spacer. Therefore, **S-PTTV** is planar and is predicted to have a much smaller band gap of 1.74 eV. According to calculations, the sulfonyl substituents in **SO_2-PTTV** only cause a small twist (10°) in the polymer's backbone, increasing the band gap by 0.10 eV.

Both substituents induce an electron-withdrawing effect, lowering both frontier orbitals by ≈0.15 eV for **S-PTTV** and ≈1.0 eV for **SO_2-PTTV**, compared to unsubstituted **H-PTTV** (Figure 1). Lower HOMO levels are beneficial for increased stability in air and are expected to produce larger open circuit voltages (V_{OC}) in OPVs.[23] At the same time, the substituents do not significantly affect the π-conjugation along the chains. The trends of MO energy vs reciprocal length of oligomers (Figure 1) are shifted along the energy axis, but are otherwise

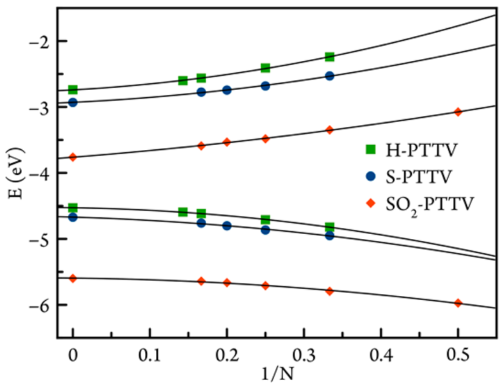


Figure 1. Calculated HOMO and LUMO energy levels of oligomers and infinite chains modeled with PBC. (N = number of repeat units).

nearly superimposable. Also, the topology of the HOMO and LUMO of the **S-PTTV**, **SO_2-PTTV** homopolymers and the (alternating) copolymer **S/SO_2-PTTV** are nearly superimposable (Figure 2). Thus, the donor−acceptor motif should not alter the electron delocalization along the backbone or the intermolecular orbital coupling.

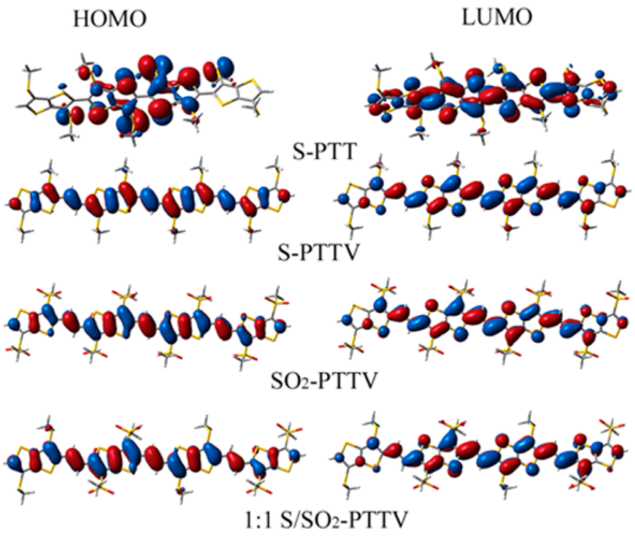


Figure 2. DFT-optimized structures of tetramers showing the topology of HOMO and LUMO.

The rigidity of the conjugated backbone is an important factor defining the material properties of polythiophenes and related structures.[24] DFT predicts a very shallow rotation barrier (≈1.5 kcal/mol) for both TT-TT and SO_2TT-vinylene connections (Figure 3). This means that nonplanar **S-PTT** could planarize due to solid state packing forces (as was in fact observed[13]). Similarly, **SO_2-PTTV**, predicted to be nearly planar in the gas phase, could adopt a twisted conformation under external factors (solvation, interchain interactions). In fact, the energy penalty for twisting the SO_2TT/vinylene dihedral angle by 50° is smaller than RT (0.6 kcal/mol at room temperature). In contrast, a much larger rotation barrier (7.9 kcal/mol per TT-vinylene connection) and thus high rigidity is predicted for **S-PTTV**. This can be attributed to the smaller size of the alkylsulfanyl group and perhaps to weak attractive S···H interactions with the vinylene protons (the calculated S···H distance is 2.80 Å).

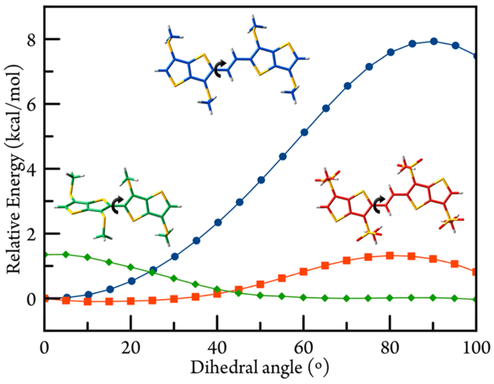
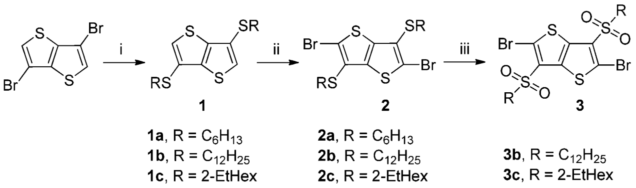


Figure 3. Energy barrier of rotation of thiophene/vinylene dihedral angles for **S-2TT** (green), **S-2TTV** (blue), and **SO_2-2TTV** (red).

Synthesis. Bisalkylsulfanyl-TT **1** was obtained from 3,6-dibromothieno[3,2-*b*]thiophene[25] by stepwise lithiation, followed by quenching of the carbanion intermediate with dialkyldisulfide (Scheme 1).[26] Brominating **1** with NBS yielded monomer **2**. We note that partial oxidation of the sulfanyl chains was occasionally observed, unless the excess of NBS is quenched before an aqueous work-up. Full oxidation of the alkylsulfanyl substituents into alkylsulfonyl was achieved with *m*-chloroperoxybenzoic acid (*m*-CPBA) to give monomer **3**.

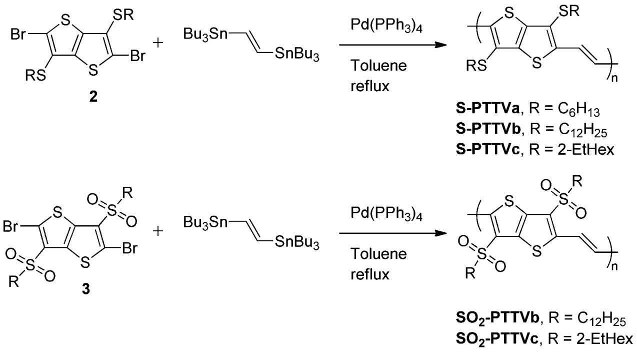
Scheme 1. Synthesis of Monomers 2 and 3[a]



[a]Key: (i) [1 equiv of nBuLi, 1 equiv of RS-SR] × 2, Et_2O, −78 to +20 °C; (ii) NBS, $CHCl_3$, −5 to +20 °C, $Na_2S_2O_3$ work-up; (iii) *m*-CPBA, $CHCl_3$, 0 to 20 °C.

Polymers were synthesized through the Stille polycondensation of monomers **2** and **3** with (*E*)-1,2-bis(tributylstannyl)-ethene followed by end-capping with an excess of the stannylated monomer, followed by iodobenzene (Scheme 2). The polymers were isolated by precipitation into MeOH and washed in a Soxhlet apparatus with EtOH, acetone, hexane, and finally extracted with chloroform and chlorobenzene.

Scheme 2. Polymerization Reaction



S-PTTV was obtained as a dark, shiny material. Hexylsulfanyl **S-PTTVa** precipitated during the reaction and displayed poor solubility, signaling the need for longer side chains. Both dodecyl-substituted **S-PTTVb** and branched 2-ethylhexyl substituted **S-PTTVc** showed high MWs, but only **S-PTTVc** was soluble enough for film spin-coating.

SO_2-PTTV gave a lower percent yield of soluble material and only low MWs could be achieved for both **SO_2-PTTVb** and **SO_2-PTTVc**. Solid state ^{13}C NMR confirmed the structure of the insoluble fractions (see Supporting Information). This low solubility is likely attributable to dipole−dipole interactions of the sulfonyl substituents.

Random copolymers have only scarcely been applied in OPVs, but they are easy to synthesize and can show increased solubility and efficiencies.[27] It is also possible to quickly realize

Table 2. Molecular Weights, Polydispersities, and UV−Vis Absorption of Synthesized Polymers

	MW (kg/mol)	PDI	yield (%)	$\lambda_{max/onset}$ solution (nm)	$\lambda_{max/onset}$ film (nm)	E_g^{opt} film^c (eV)	fwhm (cm^{-1}) soln/film
S-PTTVa	13.0	1.9	73^a	544/697	580/760	1.63	
S-PTTVb	43.4	1.3	62^b	607/730	585/770	1.61	4450/5980
S-PTTVc	42.7	2.2	62^b	610/740	608/765	1.62	4540/6250
SO_2-PTTVb	6.3	1.1	70^b	486/640	471/680	1.82	4680/5130
SO_2-PTTVc	7.6	1.3	41^b	517/625	529/720	1.72	4810/5810
S/SO_2-PTTV-1:1	27.0	2.1	75^b	597/760	594/810	1.53	4770/6540
S/SO_2-PTTV-1:2	12.9	2.5	54^b	561/748	547/755	1.64	5340/6190

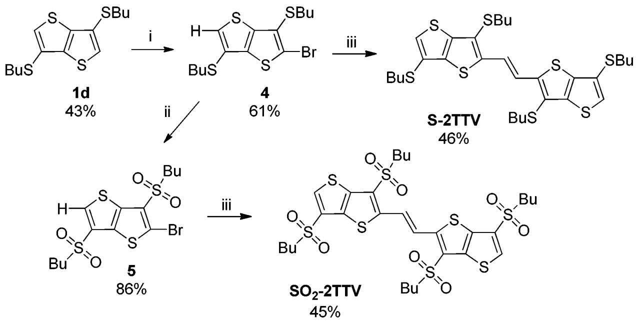
[a]Total yield of the MeOH precipitated product. [b]Yield of a polymer fraction(s) soluble in $CHCl_3$ and PhCl. [c]E_g^{opt} = 1240/λ_{edge} of film.

a series of random copolymers by simply varying the feed ratios and thereby quantify the effect of a certain unit.

S/SO_2-PTTV was synthesized by the random copolymerization of a mixture of monomers **2** and **3** with (*E*)-1,2-bis(tributylstannyl)ethene. The copolymer was soluble, with a MW that averaged those of **S-PTTV** and **SO_2-PTTV** (Table 2). The relative fraction of the sulfanyl/sulfonyl substituted TT units can be tuned by varying the ratio of the starting monomers and easily quantified by ^{1}H NMR. A 1:1 and 1:2 feed ratio of monomers **2**:**3** gave measured ratios of 1:0.88 and 1:1.6, respectively. Along with the lower MW of **SO_2-PTTV**, this indicates a reactivity preference for monomer **2** over **3**, likely due to the steric effect of the bulkier sulfonyl group and/or coordination to palladium in the catalytic complex.[28]

To gain insight into the solid-state packing of the substituted TTV systems, we synthesized two dimers by the Stille coupling of monobrominated TTs **4** and **5** with (*E*)-1,2-bis(tributylstannyl)ethene to afford dimers **S-2TTV** and **SO_2-2TTV**, respectively. Monobromination of **1d** was accomplished by lithiation (nBuLi) followed by treatment with carbon tetrabromide. **4** was then oxidized to **5** as described above (Scheme 3). Single crystals of dimer **S-2TTV** were prepared as orange needles from a mixture of ethanol, hexane, and toluene, and were subjected to X-ray analysis (Figure 4).

Scheme 3. Synthesis of Model Dimers[a]



[a]Key: (i) 1 equiv nBuli, 1 equiv CBr_4, Et_2O, −78 to +20 °C; (ii) *m*-CPBA, $CHCl_3$, 0 to 20 °C; (iii) 0.5 equiv of $Bu_3SnCH{=}CHSnBu_3$, $Pd(PPh_3)_4$, 100 °C

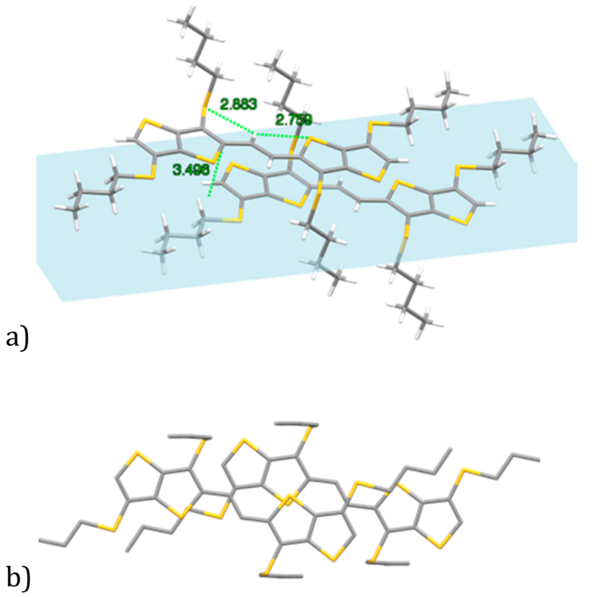


Figure 4. Crystal structure of **S-TTV** showing (a) S···H distance with vinylene hydrogen and the interplane distance and (b) the lack of π-overlap between TT units.

In accordance with the DFT calculations, the conjugated backbone of **S-2TTV** is nearly planar (TT-vinylene dihedral angle = 5.2°). The crystals formed a slipped-stacked structure with an interplane distance of 3.50 Å (Figure 4a). Importantly, the "inner" alkylsulfanyl substituents bend out of the plane at ~80°, thus protruding above and below the aromatic plane. This confirms the DFT prediction that placing this substituent in plane destabilizes the structure by ≈4 kcal/mol, compared to the optimal 83° twisted geometry (Figure S2, Supporting Information). Similar out-of-plane geometry and even larger planarization penalty was calculated for **SO2−2TTV** (Figure S2). To accommodate the out-of-plane protruding substituents, the molecules have to slip vs one another along the short molecular axis, which significantly limits π···π overlap between the TT units (Figure 4b).

Optical Properties. The UV−vis absorption spectra of the prepared polymers were studied in chloroform solution and in thin films (Figure 5, Table 2). All the polymers displayed broader absorption spectra and red-shifts of the band edge in the solid state compared to solution. The spin-coated films are highly reflective, with characteristic metallic luster (Figure 5b).

The variation of the solution absorption band with different alkyl side-chains (**S-PTTVa/b/c**) are in line with the changes in molecular weights of these polymers. Interestingly, very little difference was observed in the solid state. The absorption of solid **S-PTTVc**, λ^{edge} = 765 nm (E_g = 1.62 eV) is red-shifted from analogous alkyl-substituted poly(3,6-dihexyl)thieno[3,2-*b*]thiophene vinylene **C_6-PTTV** which showed a band edge at 700 nm (1.77 eV)[29] and from poly(3,6-dioctylsulfanylthieno-[3,2-*b*]thiophene), **SC_8-PTT**, whose band edge appears at 713 nm (1.74 eV).[13] Evidently, both the sulfanyl substituents and the vinylene spacer play a part in shrinking the band gap.

Replacing sulfanyl sides chains with sulfonyl (**SO_2-PTTV**) results in a ~0.1 eV increase of the optical band gap (720 nm, 1.72 eV), as predicted by DFT (Table 1). This increase should

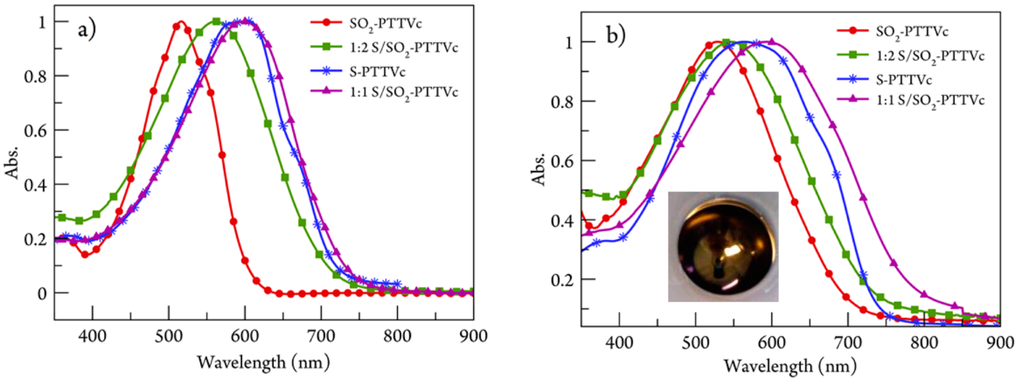


Figure 5. Absorption spectra of polymers in (a) chloroform solutions and (b) thin films (the inset shows a flask coated in a film of S-PTTVc).

in part be attributed to the low MW[36] of **SO$_2$-PTTV** (Table 2) although its lower rigidity (Figure 3) should also play a role and must be responsible for the unexpectedly large band gap in solution (1.98 eV). **SO$_2$-PTTV** displays the smallest increase in the fwhm between solution and solid state, which suggests a weakened intermolecular exciton coupling caused by the sulfonyl substituents.

Copolymer **S/SO$_2$-PTTV-1:1** retains the broad absorption (fwhm = 6540 cm^{-1}) of **S-PTTV** and shows a further lowered band gap of 1.53 eV, that can be attributed to the donor−acceptor interactions between sulfanyl and sulfonyl-substituted units. The balance between the latter appears important as the increased amount of $-SO_2$ substituted TT units in **S/SO$_2$-PTTV-1:2** increases the band gap (1.64 eV), possibly due to disrupted solid-state packing (cf. small Δfwhm$_{\text{film-sol}}$ = 850 cm^{-1}, Table 2), but also due to a lower MW.

Comparing the absorption of the dimers **S-2TTV** and **SO$_2$-2TTV,** unperturbed by the uncertainty of polymer lengths, supports the above observations. Their 0−0 transitions (450 and 444 nm, determined as a crossing of the absorption and emission curves) are 2.76 and 2.79 eV for **S-2TTV** and **SO$_2$-2TTV**, respectively (Figure 6). The sulfanyl-substituted **S-2TTV** showed a more pronounced vibronic splitting of the absorption band, as expected based on its predicted rigidity (Figure 3).

Generally, oligo- and polythiophenes are weak-to-moderate emitters, a fact attributed to the heavy atom effect of sulfur enhancing the intersystem crossing.[30] A majority of thienylenevinylene oligomers and polymers and their derivatives are almost completely nonemissive. We have earlier reported a dramatic enhancement of fluorescence in thienylene−vinylene oligomers and polymers upon the introduction of sulfanyl side chains, which was unexpected due to the additional sulfur atoms.[31] As a further surprise, we now observed that **S-PTTV** containing fused thienothiophene rings, is again nonemissive, although the model dimer **S-2TTV** exhibits a moderate emissivity (λ_{max} = 485 nm, PLQY = 15%, Figure 4). We could not find a good explanation for these variations, but we note that both alkyl-substituted PTTV (**C$_6$-PTTV**[29]) and alkylsulfanyl-substituted PTT (**SC$_8$-PTT**, PLQY = 26%[13]) are reported to show strong photoluminescence.

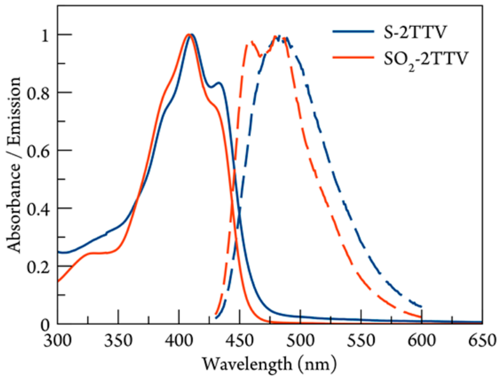


Figure 6. Absorption (—) and emission (– –) spectra of **S-2TTV** and **SO$_2$-2TTV** dimers.

In line with previous reports,[16] oxidizing the sulfanyl group into sulfonyl enhances the photoluminescence. The dimer **SO$_2$-2TTV** shows quantum yield three times larger (λ_{max} = 483 nm, PLQY = 45%) than its sulfanyl analogue **S-2TTV** (Figure 6). Moderately strong luminescence was also observed for **SO$_2$-PTTV** at λ_{max} = 585 nm (PLQY = 17%), but introducing sulfanyl-substituted units in the copolymer again quenches the luminescence, and only very week emission at 690 nm was observed for **S/SO$_2$-PTTV-1:1** (see Supporting Information).

Electrochemical Properties. The redox behavior of the synthesized polymers was studied by cyclic voltammetry (CV) for thin films drop-cast on Pt electrodes (Figure 7, Table 4).

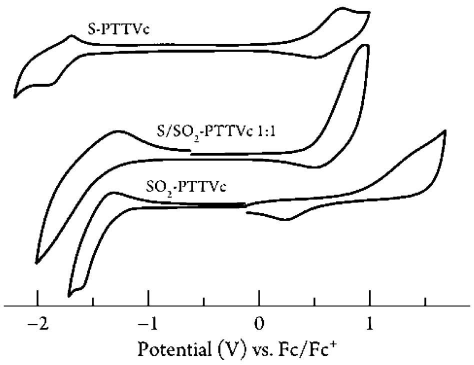


Figure 7. Cyclic voltammograms of synthesized polymers (0.1 M Bu$_4$NPF$_6$ /propylene carbonate as electrolyte; scan rate 0.1 V/s).

All three polymers show reversible reduction (n-doping) and oxidation (p-doping) waves, except for the most electron-deficient **SO$_2$-PTTV,** which revealed a quasi-reversible oxidation (ie. corresponding cathodic peaks at much more negative potentials), indicating trapping of the positive charges.

Compared to the alkyl-substituted **C$_6$-PTTV**[29] the sulfanyl substituents show a moderate electron withdrawing effect,

Table 4. Redox Potentials,[a] HOMO–LUMO Levels,[b] and Band Gaps[c] of Polymers Determined by CV of Thin Films

	E_{red} (V)	E_{ox} (V)	LUMO (eV)	HOMO (eV)	E_g^{CV} (eV)
C_6–PTTV[29]	−1.83	0.24	−2.97	−5.04	2.07
S-PTTV	−1.63	0.32	−3.17	−5.12	1.95
SO_2–PTTV	−1.20	0.91	−3.60	−5.71	2.11
S/SO_2–PTTV-1:1	−1.37	0.50	−3.43	−5.30	1.87
S/SO_2–PTTV-1:2	−1.14	0.74	−3.66	−5.54	1.88

[a] All potentials reported versus Fc/Fc^+ in 0.1 M Bu_4NPF_6/propylene carbonate. [b] Calculated from the onset of the oxidation and reduction potentials, assuming HOMO of Fc at −4.8 eV.[32] [c] E_g^{CV} = HOMO − LUMO.

shifting the oxidation and reduction of **S-PTTV** by 0.08 and 0.20 eV, respectively (Table 4). A much larger shift is observed for the sulfonyl-substituted polymer, **SO_2-PTTV** (0.67 and 0.63 V shifts for oxidation and reduction, respectively). The random copolymers **S/SO_2-PTTV-1:1** and **S/SO_2-PTTV-1:2** show the electronic effects of both monomer units with reduction and oxidation onsets between those of **S-PTTV** and **SO_2-PTTV**, giving them the smallest electrochemical gaps at 1.87 and 1.88 eV, respectively.

Device Studies. **S-PTTV** and copolymer **S/SO_2-PTTV-1:1** were tested in OFETs and OPVs, but unfortunately **SO_2-PTTV** was not soluble enough to be spin-cast into working devices.

Thin-film transistors were prepared from toluene solutions of the polymers spin-cast on Si/SiO_2 followed by the deposition of patterned Au electrodes. The output and transfer characteristics of the **S-PTTVc** transistor are shown in Figure 8. A rather low hole mobility of ~1 × 10^{-5} $cm^2/V·s$ was measured for **S-PTTVc**, and no further improvement was achieved upon annealing. The copolymer-based devices showed no transistor activity ($\mu_+ < 10^{-7}$ $cm^2/V·s$) and no n-channel activity (electron conductance) was observed for either polymers. This compares unfavorably with the reported OFETs based on **C_6-PTTV** with hole mobilities up to 1.9 × 10^{-2} $cm^2/V·s$ (for annealed films, a 40× increase from unannealed). The out-of-plane protrusion of the side chains and the resulting poor overlap between TT units, as observed in the **S-2TTV** crystals, is likely the reason for poor transistor characteristics of these materials.

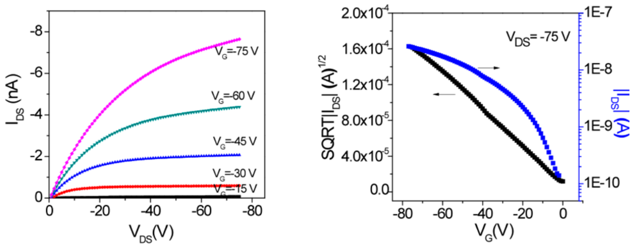


Figure 8. Output (left) and transfer (right) characteristics of transistors made from **S-PTTVc** (μ_h ~ 1 × 10^{-5} cm^2/V s).

Bulk-heterojunction solar cell devices from polymer:$PC_{70}BM$ blends were tested. Figure 9 shows the *I*–*V* curves of two of the polymers, and the photovoltaic characteristics obtained are listed in Table 5.

S-PTTV displayed slightly higher open-circuit voltages (V_{OC}) than reported for **C_6-PTTV**, as is expected due to its lower HOMO level. The trend continues for **S/SO_2-PTTV-1:1**, which has a high V_{OC} of 0.8 V.

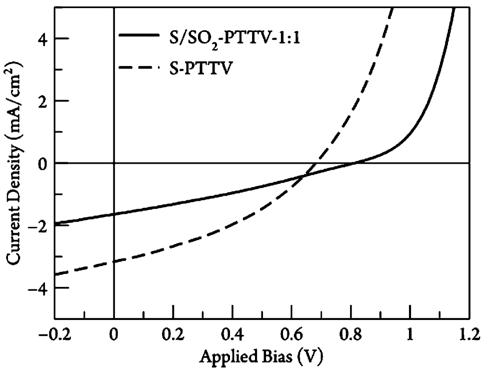


Figure 9. Current–voltage characteristics of bulk-heterojunction cells of **S/SO_2-PTTV-1:1** and **S-PTTV** in 1:1 blends with $PC_{70}BM$.

Table 5. Photovoltaic Properties of ITO/PEDOT:PSS/Polymer:$PC_{70}BM$ (1:1)/Ca/Al Devices

polymer	$HOMO_{CV}$ (eV)	I_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
C_6-PTTV[29]	−5.0	1.27	0.60	0.37	0.28
S-PTTV	−5.12	3.16	0.68	0.37	0.79
S/SO_2-PTTV	−5.30	1.64	0.82	0.29	0.39
S/SO_2-PTTV and 3% CN		4.46	0.70	0.27	0.84
S/SO_2-PTTV and 0.5% DIO		4.07	0.66	0.29	0.78

The performances of both the **S-PTTV** and **S/SO_2-PTTV-1:1** devices are limited by low short-circuit currents (I_{sc}) and fill factors (FF). This can be related to the low charge mobility seen in the transistor devices, although **C_6-PTTV**, that showed higher hole mobility in OFETs, produced even lower I_{sc} in analogous OPV devices. Poor mobilities mean more chances for recombination at the interface before the hole and electron can diffuse away and increase the serial resistance which leads to the low FFs observed.[33] Similar results were obtained with Ca vs Al electrodes, so poor charge extraction at the electrode interface is unlikely to be the issue.

Preliminary optimizations attempts for **S/SO_2-PTTV-1:1** using chloronaphthalene (CN) and 1,8-diiodooctane (DIO) additives led to improvements in the current densities, but not to FFs. The best I_{sc} (4.5 mA/cm^2) was achieved for devices with 3% CN additive, which is still half the I_{sc} seen in analogous P3HT devices without additives. The fact that the FFs did not increase suggests that while the additives may reduce the phase segregation, thereby improving the exciton dissociation, the larger interface area also increases charge recombination, leaving the low mobility of the polymers as the limiting factor.

■ CONCLUSIONS

We have reported new thienothiophene vinylene polymers whose electronic properties can be tuned by changing the oxidation state of the sulfur-containing side-chains. The sulfanyl and sulfonyl substituents show moderate and strong electron-withdrawing effects and their combination in random copolymers is a means to fine-tune the energy levels and achieve a low band gap (1.5 eV) without affecting the uniformity of the conjugated backbone. Bulk-heterojunction photovoltaics based on the **S/SO_2-PTTV-1:1** random copolymer (with $PC_{70}BM$) displayed high V_{OC} of 0.8 V, but suffered from low I_{SC} due to poor charge mobility. The latter was attributed to poor of π–π overlap between TT units caused by out-of-plane substituents, as corroborated by X-ray analysis. The oxidation state of the side chains controls the emissive properties of these materials; sulfonyl groups demonstrated dramatically increased fluorescence in dimers (PLQY of 45% vs 15% for sulfanyl) and polymers (PLQY of 17% vs ~0% for sulfanyl).

Introducing a sulfur atom in various oxidation states (sulfanyl/sulfonyl) between the alkyl chain and the conjugated backbone represents a simple and predictable method for tuning the electronic and optical properties of organic semiconductors. This method can be a welcome alternative to designing more complex donor−acceptor motifs for new polymeric semiconductors.

■ EXPERIMENTAL SECTION

All lithiation and polymerization reactions were performed under inert atmosphere, with flame-dried glassware and anhydrous solvents. 3,6-dibromothieno[3,2-b]thiophene was synthesized in four steps following literature procedures.[34]

Molecular weight measurements of the polymers were performed on a GPC PL 50 in THF at 30 °C. UV/vis absorption and photoluminescence spectra were measured in $CHCl_3$ with a JACSO V670 UV−vis−NIR spectrometer and a Varian Eclipse Fluorometer, respectively. The fluorescence quantum yields of the polymers were determined versus cresyl violet in MeOH (PLQY = 0.54), while the quantum yields of the dimers were determined versus fluorescein in 0.1 M NaOH (PLQY = 0.79). Cyclic voltammetry was performed on a CH670 potentiostat from CH-Instruments in a three-electrode cell using a propylene carbonate solution of 0.1 M $(TBA)PF_6$ as an electrolyte, at scan rates of 100 mV s^{-1}. Pt disk and Pt wire were used as the working and counter electrodes, respectively, and a Ag/AgCl or Ag/$AgNO_3$ electrode was used as the reference. All potentials were adjusted vs ferrocene (internal standard).

OPV devices were prepared on ITO-coated glass substrates that had been cleaned with detergent and rinsed by sonicating in deionized water, acetone, and finally isopropanol for 20 min each. PEDOT:PSS (Clevios P Al 4083) was spin-cast onto the ITO-coated glass at 4,000 rpm for 30 seconds and then baked at 140 °C for 10 minutes. Solutions of PC71BM and polymer in 1:1 ratios and 1 mg/mL concentrations in chlorobenzene were prepared by stirring overnight at 70 °C under inert atmosphere. The photoactive layer was spin-cast at various rates for 60 s each. Next, thermal evaporation of 5 nm of Ca and/or 100 nm of Al was performed to form the top contacts. Standard solar cell characterizations were carried out in a nitrogen environment under simulated 100 mW/cm^2 AM1.5G irradiation from a 300 W Xe arc lamp with an AM 1.5 global filter. All measurements were repeated on at least 4 devices.

DFT calculations were performed using the Gaussian 09W program at the B3LYP level with a 6-31G(d) basis set.[35] All geometry optimization calculations were started with the substituents in the anti-orientation, at 90° angles to the TT plane. The dihedral angles reported were averaged from internal TT−vinylene dihedrals in geometry-optimized oligomers. The PBC calculation for polymer were performed at the same level, with various unit cell size to enable different dihedral angles (one monomer per unit cell necessarily affords a planar polymer; two monomers allow the optimization of the dihedral angle, with alternating clock-wise/anticlockwise rotation; six monomers per units cell allows helical twisting with 60° pitch, close to the optimized 55° for S-PTT). The energy of rotation of a TT unit vs the vinylene spacer was performed on optimized dimers while freezing the dihedral angle to the second TT unit. The energy diagrams of full, 360° rotations of substituents were calculated from optimized dimers with both TT−vinylene dihedral angles frozen.

3,6-Bis(hexylsulfanyl)thieno[3,2-*b*]thiophene (1a). *n*-BuLi (0.60 mL, 1.5 mmol) was added at −75 °C to a stirring solution of 3,6-dibromothieno[3,2-*b*]thiophene (0.379 g, 0.127 mmol) in diethyl ether (20 mL) and the reaction mixture stirred for 1 h. Dihexyldisulfide (0.42 g, 1.4 mmol) was added and the reaction was allowed to warm to room temperature overnight. The next day the reaction mixture was cooled back to −75 °C and a second dose of *n*-BuLi added. After an hour, dihexyldisulfide was added and the reaction was allowed to warm to room temperature and stirred overnight a second time. The reaction was then quenched with H_2O (20 mL), the organics were washed with NH_4Cl solution (20 mL), H_2O (2 × 20 mL), then dried over Na_2SO_4, and concentrated in vacuo. The crude oil was then distilled in a Kugelrohr apparatus (170 °C, 0.16 bar) to yield pure **1a** as a colorless oil (0.319 g, 67%). ^{1}HNMR (acetone-d_6, 400 MHz): δ 7.54 (s, 2H), 2.99 (t, J = 7.2 Hz, 4H), 1.63 (m, 4H), 1.44 (m, 4H), 1.27 (m, 8H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.2, 127.0, 125.0, 34.6, 31.3, 29.6, 28.2, 22.5, 14.0. HR-MS (ESI): m/z = 373.1150 [M + 1] (calcd for $C_{18}H_{29}S_4$, m/z = 373.1147).

3,6-Bis(dodecylsulfanyl)thieno[3,2-*b*]thiophene (1b). The compound was synthesized in the same manner as described for **1a**. Kugelrohr distillation was not effective for separation, so the product was recrystallized from pentane in a −18 °C in freezer to give tan crystals in a 30% yield. ^{1}H NMR (acetone-d_6, 400 MHz): δ 7.54 (s, 2H), 3.00 (t, J = 7.2 Hz, 4H), 1.63 (m, 4H), 1.44 (m, 4H), 1.27 (m, 16H), 0.88 (t, J = 6.8 Hz, 6H). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24 (s, 2H, overlaps with $CHCl_3$), 2.90 (t, J = 7.6 Hz, 4H), 1.61 (m, 4H), 1.40 (m, 4H), 1.24 (m, 16H), 0.88 (t, J = 7.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.1, 126.9, 125.0, 34.6, 31.9, 29.6, 29.6, 29.5, 29.3, 29.1, 28.5, 22.7, 14.1.

3,6-Bis(2-ethylhexylsulfanyl)thieno[3,2-*b*]thiophene (1c). The compound was synthesized and purified as described for **1a** to give a clear oil in 78% yield. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.24 (s, 2H), 2.92 (d, J = 6.0 Hz, 4H), 1.40 (m, 9H), 1.25 (m, 9H), 0.87 (m, 12H). HR-MS (ESI): m/z = 429.1782 [M + 1] (calcd for $C_{22}H_{37}S_4$, m/z = 429.1773).

3,6-Bis(butylsulfanyl)thieno[3,2-*b*]thiophene (1d). The compound was synthesized and purified as described for **1a** to give a clear oil in 43% yield. ^{1}H NMR (acetone-d_6, 400 MHz, 25 °C): δ 7.53 (s, 2H), 2.99 (t, J = 8.0 Hz, 4H), 1.61 (m, 4H), 1.46 (m, 4H), 0.89 (t, J = 7.2 Hz, 6H). HR-MS (ESI): m/z = 317.0524 [M + 1] (calcd for $C_{14}H_{21}S_4$, m/z = 317.0521).

2,5-Dibromo-3,6-bis(dodecylsulfanyl)thieno[3,2-*b*]thiophene (2b). Thiophene **1b** (82.4 mg, 0.152 mmol) was dissolved in $CHCl_3$ (2 mL) and acetic acid (2 mL) and cooled to −40 °C. NBS (82.6 mg, 0.464 mmol) was added and the reaction warmed slowly to room temperature protected from light with foil. After being stirred for 24 h, the reaction was treated with saturated $Na_2S_2O_3$ solution (5 mL). The reaction mixture was then diluted with H_2O and extracted with $CHCl_3$ (2 × 20 mL). The solvent was removed in vacuo and the resulting product was passed through a silica plug with hexane to yield pure bromide **2b** as a white solid (77.5 mg, 73%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.89 (t, J = 7.2 Hz, 4H), 1.54 (m, 4H), 1.40 (m, 4H), 1.25 (m, 16H), 0.89 (t, J = 6.8 Hz, 6H).

2,5-Dibromo-3,6-bis(hexylsulfanyl)thieno[3,2-*b*]thiophene (2a). The compound was synthesized as described for **2b** to give an orange oil in 33% yield. ^{1}HNMR (acetone-d_6, 400 MHz): δ 2.97 (t, J = 7.2 Hz, 4H), 1.55 (p, J = 7.6 Hz, 4H), 1.44 (p, J = 7.6 Hz, 4H), 1.26 (m, 8H), 0.86 (t, J = 7.2 Hz, 6H). ^{13}CNMR ($CDCl_3$, 75 MHz): δ 139.3, 125.5, 119.1, 34.6, 31.3, 30.0, 28.2, 22.5, 14.1. HR-MS (ESI): m/z = 528.9348 [M + 1] (calcd for $C_{18}H_{27}Br_2S_4$, m/z = 528.9357).

2,5-Dibromo-3,6-bis((2-ethylhexyl)sulfanyl)thieno[3,2-*b*]thiophene (2c). Compound was synthesized as described above to give an orange oil in 42% yield. ^{1}HNMR ($CDCl_3$, 300 MHz): δ 2.87 (d, J = 3.0 Hz), 1.42 (m, 9H), 1.25 (m, 9H), 0.87 (t, J = 7.2 Hz, 12H). HR-MS (APCI): m/z = 584.9954 [M + 1] (calcd for $C_{22}H_{34}Br_2S_4$, m/z = 584.9983).

2,5-Dibromo-3,6-bis(dodecylsulfonyl)thieno[3,2-*b*]thiophene (3b). Sulfide **2b** (0.1195 g, 0.1710 mmol) was dissolved in $CHCl_3$ (5 mL) and cooled to 0 °C under nitrogen gas. MPCBA, purified from commercial reagent by washing with pH 7.5 phosphate buffer, (0.1520 g, 0.8808 mmol) was added, and the reaction mixture was allowed to warm to room temperature and stirred for 20 h. The reaction was then quenched with 0.1 M NaOH solution (25 mL), extracted with $CHCl_3$ (2 × 20 mL), and dried over Na_2SO_4. The solvent was removed in vacuo and the product was passed through a silica plug to afford pure sulfone **3b** as a white solid (0.122 g, 93%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 3.34 (t, J = 7.5 Hz, 4H), 1.75 (p, J = 7.8 Hz, 4H), 1.40 (m, 4H), 1.24 (m, 16H), 0.87 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz, 25 °C): δ 135.9, 131.0, 122.1, 55.4, 31.9 29.5, 29.5, 29.4, 29.3, 29.2, 28.9, 28.1, 22.7, 22.2, 14.1. HR-MS (ESI) m/z = 761.1021 [M + 1] (calcd for $C_{30}H_{51}Br_2O_4S_4$, m/z = 761.1031).

2,5-Dibromo-3,6-bis(2-ethylhexylsulfonyl)thieno[3,2-*b*]thiophene (3c). The compound was synthesized in the same manner as described above to give a yellow solid in 82% yield. ^{1}HNMR (acetone-d_6, 300 MHz, 25 °C): δ 3.45 (d, J = 6.0 Hz, 4H), 1.44 (m, 10H), 1.24 (m, 8H), 0.86 (t, J = 7.2 Hz, 12H). ^{13}CNMR ($CDCl_3$, 125 MHz): δ 135.8, 131.8, 122.0, 58.8, 34.6, 32.5, 28.2, 25.9, 22.6, 14.0, 10.3. HR-MS (ESI): m/z = 648.9771 [M+1] (calcd for $C_{22}H_{35}Br_2O_4S_4$, m/z = 648.9779).

2-Bromo-3,6-bis(butylsulfanyl)thieno[3,2-*b*]thiophene (4). 3,6-Bis(butylsulfanyl)thieno[3,2-*b*]thiophene (0.1667 g, 0.5266 mmol) was cooled to −75 °C in dry Et_2O. nBuLi was added dropwise and the reaction was stirred for 40 min at −75 °C before being warmed to −10 °C for 1 h. The reaction mixture was then cooled back to −75 °C, and carbon tetrabromide (0.1665 g, 0.5021 mmol), dissolved in 1 mL of dry Et_2O, was added dropwise. After 2 h, the reaction mixture was quenched with H_2O (10 mL), diluted in Et_2O (25 mL), washed with H_2O and $NaHCO_3$ solution, and then dried over Na_2SO_4. The product was purified by silica-gel column chromatography with hexane and $CHCl_3$ as eluent (1:0 to 9:1 gradient) to afford a yellow oil (0.126 g, 61% yield). ^{1}HNMR (acetone-d_6, 400 MHz, 25 °C): δ 7.65 (s, 1H), 2.985 (t, J = 7.2 Hz, 2H), 2.978 (t, J = 7.2 Hz, 2H) 1.61 (m, 4H), 1.46 (m, 4H), 0.895 (t, J = 7.2 Hz, 3H), 0.870 (t, J = 7.2 Hz, 3H).

2-Bromo-3,6-bis(butylsulfonyl)thieno[3,2-*b*]thiophene (5). Compound was synthesized in the same manner as described for compound **3** to give a yellow solid in 86% yield. ^{1}HNMR (acetone-d_6, 300 MHz, 25 °C): δ 8.59 (s, 1H), 3.50 (t, J = 7.5 Hz, 2H), 3.39 (t, J = 7.8 Hz, 2H), 1.72 (m, 4H), 1.45 (m, 4H), 0.89 (t, J = 6.9 Hz, 6H).

General Procedure for Stille Polycondensation Polymerization. The TT and (E)-1,2-bis(tributylstannyl)ethene monomers were weighed out and transferred to a pear-shaped flask and placed under a stream of nitrogen gas. $Pd^0(PPh_3)_4$ (10 mol %) was weighed out into a dry 25 mL Schlenk tube in a glovebox. The monomer mixture was transferred to the reaction flask, rinsing with dry toluene (2 mL). The mixture was degassed by freeze−pump−thaw (2 × 15 min at −75 °C). The reaction was then heated to reflux (110 °C) and sealed under nitrogen gas. The polymerization was monitored by UV over 48 h, but no further shift in the UV absorption onset was observed after 15 h. The reaction product was then precipitated by dropwise addition into MeOH (100 mL) and collected by filtration on PTFE membrane. The polymers are purified by Soxhlet extraction by sequential washing with ethanol, acetone, and hexane and finally collected in chloroform or chlorobenzene.

(*E*)-1,2-Bis(3,6-bis(butylsulfanyl)thieno[3,2-*b*]thiophen-2-yl)ethene (S-2TTV). **4** (49.9 mg, 0.126 mmol) and (E)-1,2-bis(tributylstannyl)-ethene (33.3 μL, 0.0632 mmol) were loaded into a 25 mL Schlenk tube. Dry toluene (2 mL) was added and the tube was flushed with N_2 before the addition of $Pd(PPh_3)_4$ (15.5 mg, 0.0134 mmol). The reaction was heated to 100 °C, sealed under N_2, and stirred overnight. After cooling, the reaction mixture was diluted in EtOAc and washed with NH_4Cl solution (50 mL). The organics were then washed with 1 M KF solution (2 × 20 mL) with vigorous shaking. The combined KF fractions were extracted with EtOAc and the organic phases dried with Na_2SO_4. The organics were then filtered through cotton and the solvent removed in vacuo. The product was flashed through silica with hexane and $CHCl_3$ as eluent (9:1) and further purified by recrystallization from hexane to afford 18.8 mg (46% yield) of **S-2TTV** as an orange powder. ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.49 (s, 2H), 7.22 (s, 2H), 2.887 (t, J = 7.2 Hz, 4H), 2.822 (t, J = 7.2 Hz, 4H), 1.50 (m, 16H), 0.863 (t, J = 7.2 Hz, 6H), 0.830 (t, J = 6.9 Hz, 6H). ^{13}CNMR (dimethyl sulfoxide-d_6, 500 MHz, 83 °C): δ 144.9, 143.7, 137.8, 128.2, 125.2, 124.0, 122.0, 35.1, 34.1, 32.0, 31.7, 21.42, 21.27, 13.67, 13.64. HR-MS (ESI): m/z = 657.0978 [M + 1] (calcd for $C_{30}H_{41}S_8$, m/z = 657.0968). Single crystals were grown by dissolving **S-2TTV** in a hot toluene/hexane/ethanol mixture and cooling overnight.

(*E*)-1,2-Bis(3,6-bis(butylsulfonyl)thieno[3,2-*b*]thiophen-2-yl)ethene (SO_2-2TTV). The same procedure as above was used with **5** as starting material. The product was flashed through silica with DCM, concentrated, then recrystallized from propanol and centrifuged to remove the propanol supernatant to afford 30.2 mg (45% yield) of pure **SO_2-2TTV** as an orange powder. ^{1}HNMR ($CDCl_3$, 300 MHz, 25 °C): δ 8.20 (s, 2H), 8.01 (s, 2H), 3.24 (t, J = 8.1 Hz, 8H), 1.79 (m, 8H), 1.46 (m, 8H), 0.937 (t, J = 7.2 Hz, 6H), 0.913 (t, J = 7.2 Hz, 6H). ^{13}CNMR (dimethyl sulfoxide-d_6, 500 MHz, 83 °C): δ 148.5, 139.9, 139.2, 134.0, 132.6, 129.7, 123.9, 56.8, 55.9, 24.7, 24.7, 21.08, 21.05, 13.56, 13.55. HR-MS (ESI): m/z = 785.0569 [M + 1] (calcd for $C_{30}H_{41}O_8S_8$, m/z = 785.0562). Mp >300 °C (dec.)

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of the synthesized polymers (solution and solid state) and monomer precursors, emission spectra of **SO_2-PTTV** and **S/SO_2-PTTV-1:1**. CV of **S/SO_2-PTTV-1:2**, additional device performance data. DFT optimized geometries of calculated polymers, AFM images of polymer blend morphology, and an X-ray crystallographic data (.cif) file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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