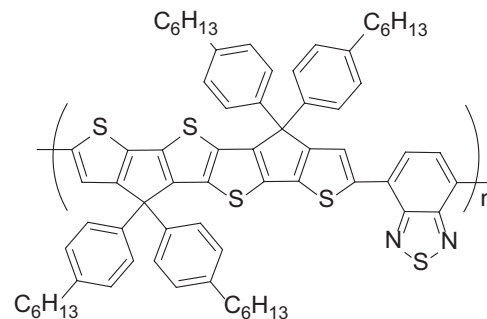


Synthesis of a Novel Fused Thiophene-thieno[3,2-b]thiophene-thiophene Donor Monomer and Co-polymer for Use in OPV and OFETs^a

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The synthesis of a novel fused hexacyclic electron rich monomer incorporating thieno[3,2-b]thiophene is reported and characterized by single crystal X-ray diffraction. Suzuki co-polymerization with benzothiadiazole (BT) afforded a novel low band-gap polymer **P4TBT** with high molecular weights and good solution processability. Bulk heterojunction solar cell devices using the **P4TBT** and [70]PCBM gave power conversion efficiencies of 2.5%. Top-gate, bottom-contact field effect transistors (FETs) using **P4TBT** displayed high hole mobilities of $0.07 \text{ cm}^2 \cdot \text{Vs}^{-1}$ demonstrating the suitability of the novel monomer and polymer for use in high performing organic electronic devices.



P4TBT

Introduction

The potential use of conjugated polymers for large area solution deposited solar cell and thin film transistor devices have prompted much interest in the area. In organic photovoltaics (OPV) research, the most promising class of conjugated polymers are the donor-acceptor (D-A) alternating co-polymers, which allow access to planar low band-

gap materials through HOMO and LUMO orbital hybridization.^[1–3] In recent years, D-A co-polymers have been used to fabricate solar cells in excess of 7% power conversion efficiency (PCE).^[4,7] Field effect transistors (FETs) with hole mobilities exceeding $1 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ ^[5,6,8] have also been demonstrated, which appear to utilize intermolecular self-assembling properties enhanced by the dipoles along a D-A backbone. The correct choice of electron rich donor and electron poor acceptor monomers, as well as their solubility, is critical to ensure the resulting polymer is solution processable and possesses the desired energy levels. Several groups have reported the synthesis and use of indacenodithiophene (IDT) as a planar electronic rich donor molecule in D-A co-polymers for use in OPV and FET devices.^[9–11] Co-polymerization of this unit with benzothiadiazole (BT) has yielded both efficient OPV devices giving in excess of 6% PCE when blended with [70]PCBM, and extremely high hole mobility polymers depending on the choice of side chain.^[5,12,13] We envisaged that replacement of the central

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phenyl unit of IDT with thieno[3,2-*b*]thiophene would enhance the electron donating properties of the monomer unit. Furthermore, the increased size and planarity of the monomer unit could encourage π - π stacking of polymer chains, which could facilitate hopping and result in increased charge carrier mobility.^[14,15]

Results and Discussion

Synthesis

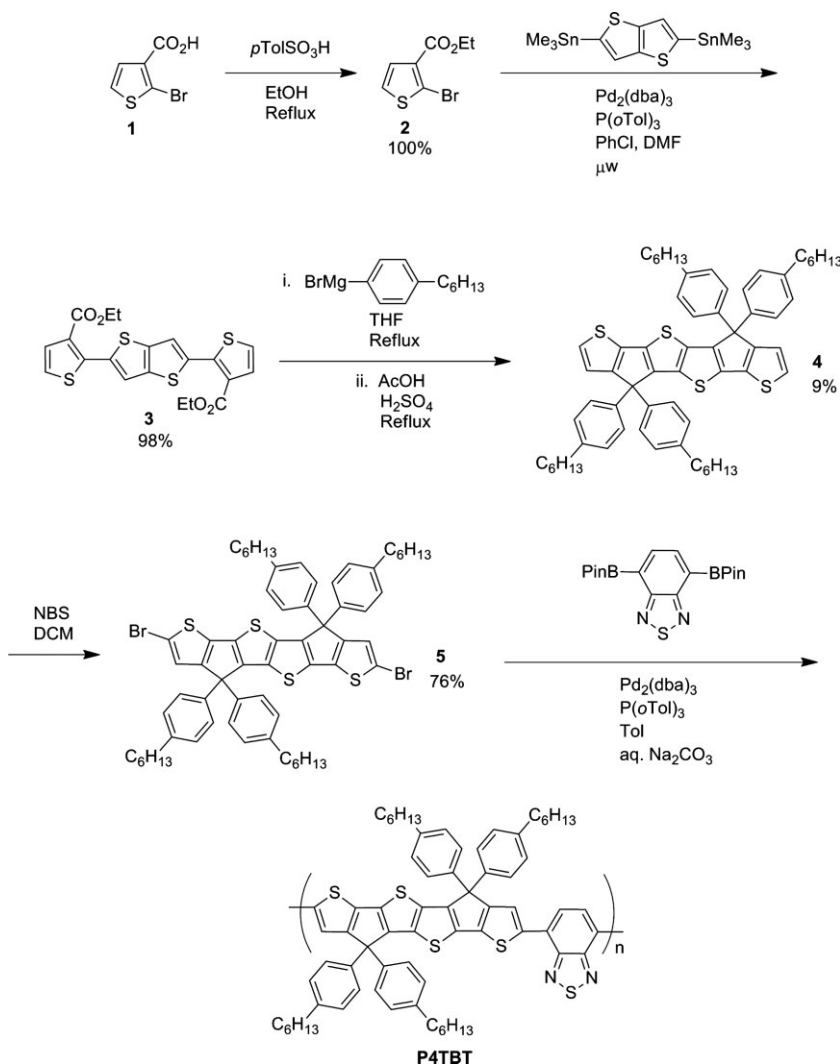
The synthesis of the novel donor molecular is outlined in Scheme 1. Esterification of commercially available 2-bromo-3-carboxylic acid **1** afforded ethyl 2-bromo-3-thiophenecarboxylate **2** in quantitative yield. A microwave assisted Stille coupling of **2** and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene was used to synthesize diethyl

2,2'-(thieno[3,2-*b*]thiophene-2,5-diyl)bis(thiophene-3-carboxylate), which is isolated as an orange solid in excellent yield. Dropwise addition of a solution of freshly prepared 4-*n*-hexylphenyl magnesium bromide, followed by an acid catalyzed ring closure using conditions similar to those reported previously for the synthesis of IDT gave access to the novel fused hexacyclic ring system **4**.^[11] The low yield for the cyclization is due to some degree of oligomerization upon addition of the sulfuric acid, as a significant amount of dark insoluble plastic-like material is obtained on work up. Removal of this by-product, however, is simple and column chromatography affords the pure product. Attempts at optimization of this ring-closure are ongoing. Bromination using NBS and subsequent recrystallization from acetone affords the novel monomer **5** in good yields.

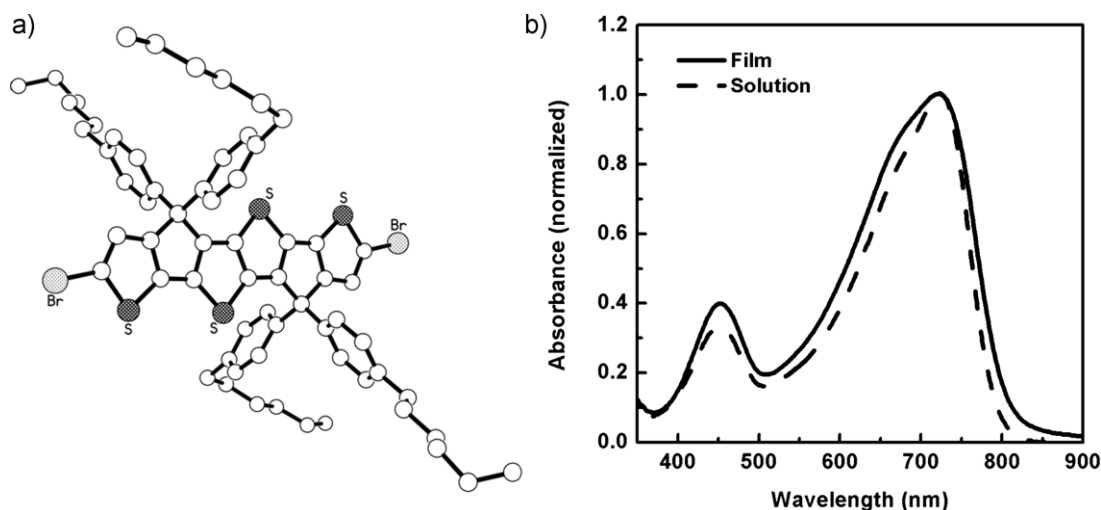
A single crystal of **5** was grown from a hexane solution and analyzed by single crystal XRD to confirm both the structure and planar nature of the six-fused ring donor monomer (Figure 1a). It is interesting to note that this novel donor system is effectively two planar fused cyclopentadithiophene moieties, which have demonstrated much success in the field of organic electronics.^[16]

Polymerization

To investigate the potential of this novel donor molecule in a conjugated polymer, 2,1,3-BT was chosen as the acceptor to allow for direct comparison with the previously reported IDT-BT polymers.^[13] Suzuki coupling of **5** with 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) **6** using previously reported conditions^[5] afforded the novel polymer **P4TBT** as a dark solid. The polymer was purified by Soxhlet extraction using acetone and hexane, in order to remove low molecular weight oligomers, and finally chloroform, in which it was fully soluble. Residual catalytic palladium impurities were removed by vigorously heating and stirring a chloroform solution of the polymer in the presence of aqueous sodium diethyldithiocarbamate.^[17] The molecular weight of the polymer was estimated by GPC using PS standards and chlorobenzene as eluent to be a satisfactory $\bar{M}_n \approx 19$ kDa and $\bar{M}_w \approx 50$ kDa. The polymer is readily soluble in organic solvents such as CHCl_3 and



■ Scheme 1. Synthetic route towards novel 4T monomer and polymer.



■ Figure 1. (a) The molecular structure of **5**; (b) Solution (CHCl_3) and thin film (PhCl) UV-Vis absorption spectra of **P4TBT** polymer.

chlorobenzene which allows for facile solution processing (Table 1).

Figure 1b shows the solution (chloroform) and thin film (spun from chlorobenzene) UV-Vis absorption spectra of **P4TBT**. The polymer absorbs over a broad range of wavelengths indicating its suitability for use in OPV. The absorption maxima in both solution and thin film is 729 nm. The HOMO energy level was measured by PESA (Photo Electron Spectroscopy in Air) to be -5.2 eV, which is approximately 0.2 eV higher in energy than the phenyl containing IDT-BT copolymer. This implies that the novel donor monomer is significantly more electron donating than the IDT analogue. This is to be expected, due to the inclusion of the electron rich thieno[3,2-*b*]thiophene unit at the expense of the more electron poor phenyl unit. It is interesting to note that there is very little change in the absorption spectra on going from solution to film; with the exception of a slight broadening of the absorption, implying that the polymer is not particularly crystalline in the solid state, presumably due to the steric bulk of the hexylphenyl side-chains. The absorption onset at ≈ 820 nm (1.5 eV) demonstrates that this is an extremely narrow band gap polymer.

Performance in OFETs

Top-gate, bottom-contact devices were fabricated on glass with PFBT treated Au S/D electrodes, a CYTOP dielectric and an aluminium gate. Polymer films were spin cast at 2000 rpm from hot chlorobenzene solution ($5 \text{ mg} \cdot \text{mL}^{-1}$) and thermally annealed for 10 min at either 150 or 200 °C. The output and transfer characteristics of a typical device annealed at 200 °C are shown in Figure 2(a) and (b). The novel polymer displayed impressive saturated field effect mobilities in the range of $0.05\text{--}0.07 \text{ cm}^2 \cdot \text{Vs}^{-1}$, with an on/off ratio of $\approx 10^4$. The samples annealed at 150 °C showed a small amount of hysteresis in the output characteristics. Annealing at the higher temperature of 200 °C completely eliminated the hysteresis presumably due to improved thin film morphology. The polymer solution suffered from poor wettability on the substrate indicating that alternative device configurations with higher surface energy substrates could be more suited. Despite this, these values are significantly higher than the analogous IDT-BT copolymer with identical hexylphenyl side-chains, although it should be mentioned that a different device architecture was used.^[10] The inclusion of the central thieno[3,2-*b*]thiophene

■ Table 1. Properties of **P4TBT**.

\bar{M}_n [kDa] ^{a)}	\bar{M}_w [kDa] ^{a)}	PDI ^{a)}	$\lambda_{\text{max soln.}}$ [nm] ^{b)}	$\lambda_{\text{max film}}$ [nm] ^{c)}	HOMO [eV] ^{d)}	LUMO [eV] ^{e)}	Energy gap [eV] ^{f)}
19	50	2.6	729	729	-5.2	-3.7	1.5

^{a)}Determined from GPC using PS standards and PhCl as eluent; ^{b)}Measured in dilute chloroform solution; ^{c)}Spin-coated from $5 \text{ mg} \cdot \text{mL}^{-1}$ PhCl solution; ^{d)}Measured by UV-PES; ^{e)}Estimated by addition of absorption onset to the HOMO; ^{f)}Determined from absorption onset of thin film UV-Vis spectrum.

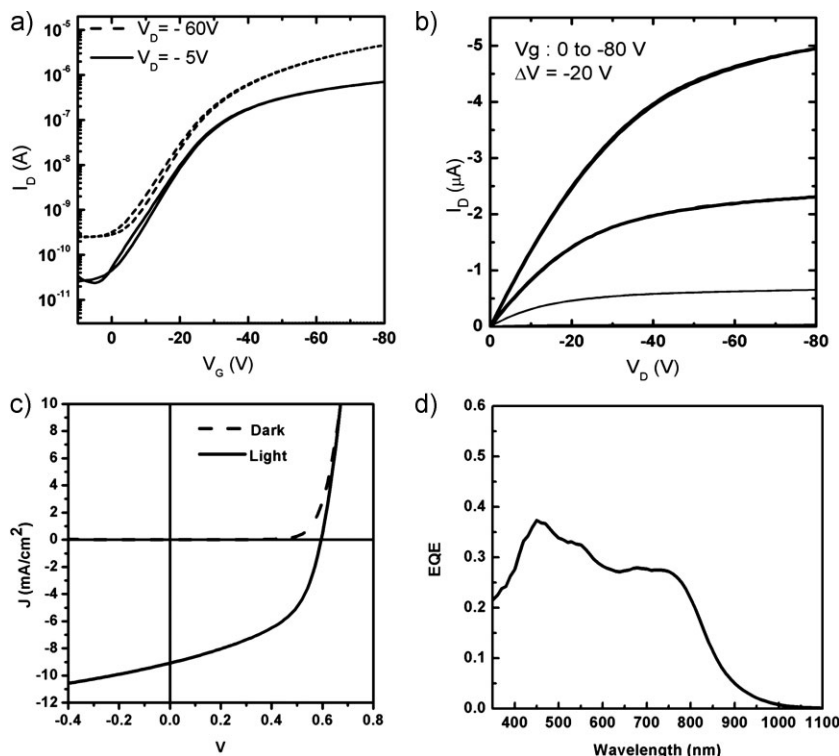


Figure 2. (a) Transfer characteristics of OFET device annealed at 200 °C; (b) Output characteristics of OFET device annealed at 200 °C; (c) J - V curve of OPV device; (d) EQE spectra of OPV device.

a good match with the polymer UV-Vis absorption spectra. However, despite its broad range, the EQE does not exceed 40% at any wavelength. Due to the similarity in the LUMO energy levels of this polymer and IDT-BT, it is unlikely that the low EQE is due to an insufficient energetic offset between the polymer and the fullerene.^[18] A low FF is often indicative of undesirable nanoscale morphology, which we believe is the cause of the low measured EQE. In materials with similar solubilizing groups, the use of additives has greatly improved the FF of the device and it is expected that further optimization is possible for this polymer.^[12]

Conclusion

A novel fused hexacyclic thiophene-based donor monomer has been synthesized and characterized by single crystal X-ray diffraction. Co-polymerization of the monomer with benzothiadiazole afforded a high molecular weight novel low band-gap polymer. Top gate, bottom contact OTFT devices show promising mobilities in both the linear and saturated regime,

with values approaching 0.1 cm²/Vs. Initial BHJ solar cell devices in combination with [70]PCBM give promising power conversion efficiencies of 2.5%, which is mostly attributed to a high short circuit current due to its narrow band-gap and broad absorption. It is anticipated that variation of the solubilizing alkyl chains and/or the co-monomer will afford a new family of donor-acceptor conjugated polymers with great potential in the field of organic electronics.

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has extended the planarity of the polymer which is likely the cause of the improved relative mobility. Replacement of hexylphenyl side chains with long linear alkyl side chains in the IDT-BT system has resulted in hole mobilities of over 1 cm²/Vs due to its greater crystallinity.^[5] It is anticipated that replacement of the phenylhexyl side-chains with long linear alkyl chains in the novel 4TBT system will have similar results, and efforts in this direction are ongoing.

Performance in OPV Devices

Solar cell devices were made with device structure ITO:PEDOT/PSS:Active Layer:LiF:Al. An ODCB solution of 1:4 polymer:[70]PCBM was spin coated to create the active layer with a thickness of 80 nm, followed by evaporation of the back contacts. Figure 2(c) shows the current density-voltage characteristics of the solar cell under AM 1.5 conditions. The PCE was found to be 2.5% PCE, with an open circuit voltage of 0.59 and a J_{sc} of -9.1 mA · cm⁻². A fairly low fill factor of 0.49 was obtained, which is the main reason for the modest device efficiency. The EQE spectra are shown in Figure 2(d). The broad coverage of the EQE over a large portion of the solar spectrum results in a good J_{sc} under illumination. The [70]PCBM contribution to the device photocurrent can clearly be seen by the maxima at ≈ 450 nm, with the remainder of the EQE spectra having

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