Improved Photovoltaic Performance of a Semicrystalline Narrow Bandgap Copolymer Based on 4H-Cyclopenta[2,1-b:3,4-b’]dithiophene Donor and Thiazolo[5,4-d]thiazole Acceptor Units

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ABSTRACT: A solution processable narrow bandgap polymer composed of alternating 2,5-dithienylthiazolo[5,4-d]thiazole and asymmetrically alkyl-substituted 4H-cyclopenta[2,1-b:3,4-b’]dithiophene units (PCPD-TDTzTz) was synthesized by Suzuki polycondensation and the donor–acceptor copolymer was thoroughly characterized. Thermal analysis and X-ray diffraction studies disclosed the semicrystalline nature of the material. When blended with PC71BM and integrated in bulk heterojunction organic solar cells, a moderate power conversion efficiency of 2.43% under AM 1.5 G (100 mW/cm2) conditions was obtained. However, upon purification of the semiconducting copolymer by preparative size exclusion chromatography, a noticeable rise in power conversion efficiency to 4.03% was achieved. The purified polymer exhibited a relatively high field-effect carrier mobility of $1.0 \times 10^{-3} \text{cm}^2/(\text{V s})$. The active layer morphology was explored by atomic force microscopy and transmission electron microscopy studies, showing phase segregation on the nanometer scale.

KEYWORDS: 4H-cyclopenta[2,1-b:3,4-b’]dithiophene, thiazolo[5,4-d]thiazole, alkyl side chains, semicrystallinity, preparative GPC, bulk heterojunction organic solar cells

INTRODUCTION

Organic (polymer) solar cells (OSC’s) offer great opportunities as renewable energy sources, as they combine unique features such as the potential for low cost large-area fabrication, solution processability, aesthetics, reduced weight, and mechanical flexibility.1 Bulk heterojunction (BHJ) OSC’s based on regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester (PC61BM) as active layer donor and acceptor materials, respectively, have achieved power conversion efficiencies (PCE’s) of 4–5%.1–3 The main problem associated with the P3HT:PC61BM combination is the mismatch between the OSC absorption window and the terrestrial solar spectrum due to the relatively large bandgap of the polythiophene donor polymer and the limited absorption width of the material blend. The most popular approach to obtain lower bandgap structures is based on copolymerization of (heteroaromatic) donor and acceptor moieties.1 Incorporating alternating electron rich and electron deficient subunits...

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produces a significant decrease in the bandgap (and a concomitant red-shifted absorption) due to intramolecular charge transfer (ICT).

During the last five years, 4H-cyclopenta[2,1-b:3,4-b′]-dithiophene (CPDT) has emerged as an attractive building block for organic photovoltaics (OPV), combining good electron-donating properties, a rigid coplanar structure favoring \( \pi-\pi \) intermolecular interactions, and straightforward side-chain manipulation to influence solubility and processability. Although a standard workhorse material among the high efficiency low bandgap copolymers has not been defined yet, PCPDTBT, consisting of alternating CPDT and 2,1,3-benzothiadiazole (BT) units, is undoubtedly the most studied and best defined material within this subclass.\(^4\)

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The complementary dibromo-TzTz monomer, 2,5-bis(3′-hexylthiophene-2′-yl)thiazolo[5,4-d′]thiazole (2), was obtained through a condensation reaction between 3-hexylthiophene-2-carbaldehyde and dithioxamide and subsequent dibromination with N-bromosuccinimide (NBS).\(^{31,36}\) The additional hexyl side chains on both thiienyl constituents were introduced to improve solubility. The PCPDT-DTTzTz copolymer was then produced by means of a Suzuki polymerization reaction in toluene (Scheme 2).\(^{3,35}\) End-capping was performed by sequential addition of phenylboronic acid and bromobenzene. The polymer was purified by successive Soxhlet extractions (with methanol, n-hexane, and CHCl\(_3\), respectively) and finally precipitated from methanol as a dark, almost black powder. The material was found soluble in a number of common organic solvents such as chloroform, chlorobenzene, and tetrahydrofuran. The number-average molecular weight (\(M_n\)) after purification, as determined by analytical size exclusion chromatography (SEC) in tetrahydrofuran, was 1.7 × 10\(^4\) g/mol, with a polydispersity (PDI) of 2.9. Reproducibility of the

![Scheme 1. Three-Step Synthetic Approach to Asymmetrically Functionalized 4H-Cyclopenta[2,1-b:3,4-b′]-dithiophenes](image)

The final opto-electronic features of the low bandgap material,\(^{29,32-34}\) with a major impact on blend morphology, flexibility in the design of the side chains is of high value. In this procedure, variability is introduced at the stage of the ketone derivative. With the aim of balancing polymer crystallinity (toward high charge-carrier mobility) and solubility/processability (toward optimum blend morphology), a CPDT building block with a linear octyl and a branched 2-ethylhexyl side chain was prepared. CPDT-bisboronate monomer 1 (Scheme 2), required for Suzuki polycondensation,\(^{35}\) was synthesized by lithiation of the dibrominated CPDT precursor and reaction with 2-isopropanyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

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**RESULTS AND DISCUSSION**

**Synthesis and Characterization.** The cyclopentadithiophene building block was synthesized using a method recently developed in our group (Scheme 1).\(^{30,31}\) This three-step synthetic protocol allows to synthesize asymmetrically disubstituted CPDT units. As the side chains are of crucial importance for...
Suzuki polycondensation reaction was satisfactory, as similar molecular weights and PDI’s were observed for two other polymerization trials.

Thermogravimetric analysis (TGA) experiments in inert atmosphere showed degradation sets in at 400 °C (Figure S1). No weight loss was observed up to 350 °C. Differential scanning calorimetry (DSC) experiments from room temperature up to 300 °C at a heating rate of 20 K/min (after cooling from 300 °C at the same rate) showed a small step in heat capacity around 10 °C (0.05 J/g·K), followed by a broad exotherm (1 J/g) that gradually evolved to a broad endotherm with a peak maximum at 262 °C (11 J/g) (Figure 1, Table 1). These events can be attributed to a glass transition, cold crystallization and crystal reorganization, and melting of the crystals, respectively. Upon cooling at 20 K/min, a crystallization peak was seen with a maximum at 231 °C (10 J/g). Summarily, DSC experiments indicated the polymer is semicrystalline, showing a small $T_g$ and a broad melting endotherm. To confirm this semicrystallinity, XRD analysis of the polymer powder was performed. The XRD spectrum (Figure 2) showed the presence of some crystalline phase, as demonstrated by the appearance of several broad peaks. For a series of four alternating CPDT-based copolymers different from the ones synthesized here, Shim et al. 19 found glass transition temperatures of 103−107 °C. No indications of the presence of a crystalline phase were mentioned in those cases.

UV−vis absorption spectra of the polymer in solution (CHCl₃) and film are plotted in Figure 3. Intramolecular charge transfer between the electron rich CPDT and the electron poor TzTz units in the polymer backbone induces a narrow bandgap and a reasonably broad absorption that covers the 450−700 nm range. In chloroform, the spectrum showed a maximum absorption at 580 nm (with a vibronic shoulder at the low-energy side). In film, the peak bandwidth was broader, and a noticeable fine-structure appeared at the high-wavelength side, suggesting local structural order. The optical bandgap in film was determined to be around 1.79 eV (Table 1). Compared to the well-known bis(2-ethylhexyl)-substituted PCPDTBT donor polymer ($E_g$ 1.46 eV), the optical bandgap is significantly larger and the overlap with the solar spectrum is somewhat reduced, in particular at the near-IR side.

The cyclic voltammogram (Figure S2) of a thin film of PCPDT-DTTzTz displayed quasi-reversible oxidation and reduction processes during the first potential scan. Upon repeated scanning, the currents associated with these features reduced slowly. The onsets of oxidation and reduction occurred at 0.38 V and −1.42 V vs Ag/AgNO₃, respectively. The corresponding energy levels for the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are −5.31 eV and −3.51 eV, respectively, very close to the values reported by Brabec et al. for PCPDTBT (−5.3 and −3.57 eV). The resulting electrochemical bandgap is 1.80 eV. This value is almost identical to the observed optical bandgap (1.79 eV) (Table 1).

**Figure 3.** UV−vis absorption spectra of PCPDT-DTTzTz in chloroform solution (black) and in film (green).

**Table 1.** Thermal, Electrochemical, and Optical Properties of PCPDT-DTTzTz

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (°C)</th>
<th>Value (eV)</th>
<th>Value (eV)</th>
</tr>
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<tr>
<td>$T_g$</td>
<td>10</td>
<td>−5.31</td>
<td>1.80</td>
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<tr>
<td>$T_c$</td>
<td>262</td>
<td>−3.51</td>
<td>1.79</td>
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<tr>
<td>$T_m$</td>
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<td></td>
</tr>
<tr>
<td>$T_d$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>HOMO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LUMO</td>
<td></td>
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</table>

*a* In film.

**BHJ Organic Solar Cells.** When the PCPDT-DTTzTz polymer, as obtained after Soxhlet extraction and precipitation (batch A), was blended with PC_{71}BM in a 1:3 w/w ratio (in chlorobenzene), the resulting solar cell device (ITO:PEDOT/PSS:active layer:Ca−Ag) showed a moderate performance with an open circuit voltage ($V_{oc}$) of 0.58 V, a fill factor (FF) of 0.47, a short-circuit current density ($J_{sc}$) of 9.0 mA/cm², and a
resulting PCE of 2.43% under air mass 1.5 global illumination conditions (AM 1.5G; 100 mW/cm²) (Table 2, Figure 4).

As polymer molecular weight (distribution) and purity are essential parameters influencing the opto-electronic properties and the final solar cell outcome, purification and fractionation of the PCPDT-DTTzTz copolymer were pursued by preparative SEC. An additional advantage of this technique is that it can somehow remediate the significant batch-to-batch variations often observed for transition-metal catalyzed polymerization reactions (mainly Suzuki/Stille). Unfortunately, limited solubility of the material (at a concentration of 20 mg/2 mL) in the eluent (CHCl₃) somewhat hampered effective fractionation due to polymer aggregation (see Figures S3 and S4). Two purified polymer fractions (B and C, Table 2) were obtained, with slightly varying $M_n$ and PDI. Solar cell devices constructed from these materials showed a significant increase in PCE of more than 1% (to 3.5% for batch C, Table 2), by noticeable improvement of all three parameters ($V_{oc}$, $J_{sc}$, and FF). Upon mixing both purified batches (batch D = 1:2 ratio of B and C, Table 2), mainly affecting the PDI, the solar cell performance was even further improved, showing a PCE of 4.03% ($V_{oc}$ 0.67 V, FF 0.54, $J_{sc}$ 11.13 mA/cm²) (Table 2, Figure 4). As the experimentally observed $V_{oc}$ fits rather well with the theoretically expected value, the PCE seems to be $V_{oc}$ limited for this material. 4,6 The PCE was noticeably higher than for a series of four different PCDT-X:PC₆₁BM combinations earlier reported by Shim and co-workers. 19

The thin film morphology of the BHJ mixture was examined by atomic force microscopy (AFM) and transmission electron microscopy (TEM) (Figure 5). The purified PCPDT-DTTzTz polymer formed homogeneous, well-distributed blend films with PC₇₁BM, indicating good miscibility (or compatibility) with phase segregation on the nanometer scale.

**CONCLUSION**

We have synthesized a novel performant poly[(4H-cyclopenta-[2,1-b:3,4-b']dithiophene)-alt-(2,5-dithienylthiazolo[5,4-d]-thiazole)] narrow bandgap copolymer PCPDT-DTTzTz, with

<table>
<thead>
<tr>
<th>batch</th>
<th>$M_n$ (g/mol)</th>
<th>PDI</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
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<tr>
<td>A</td>
<td>$1.7 \times 10^4$</td>
<td>2.9</td>
<td>0.58</td>
<td>9.0</td>
<td>0.47</td>
<td>2.43$^a$</td>
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<tr>
<td>B</td>
<td>$1.7 \times 10^4$</td>
<td>2.3</td>
<td>0.63</td>
<td>10.33</td>
<td>0.51</td>
<td>3.34$^b$</td>
</tr>
<tr>
<td>C</td>
<td>$1.5 \times 10^4$</td>
<td>2.2</td>
<td>0.63</td>
<td>10.37</td>
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<tr>
<td>D</td>
<td>$1.4 \times 10^4$</td>
<td>2.4</td>
<td>0.67</td>
<td>11.13</td>
<td>0.54</td>
<td>4.03$^{bc}$</td>
</tr>
</tbody>
</table>

$^a$Unpurified polymer. $^b$Purification by preparative SEC. $^c$Mixture of B and C in 1:2 ratio.

Figure 4. $J$-$V$ characteristics of photovoltaic devices fabricated from different batches of PCPDT-DTTzTz (blended with PC₇₁BM in a 1:3 w/w ratio).

Figure 5. Topographic AFM images of spin-coated PCPDT-DTTzTz:PC₇₁BM films (measurements on a solar cell device), with a rms roughness value of 7.3 nm (1 μm × 1 μm) (a) and BFTEM-image (with diffraction pattern in inset) of the PCPDT-DTTzTz:PC₇₁BM (1:3) film (b).
asymmetrical alkyl substitution on the CPDT building blocks and additional hexyl side chains on the thienyl subunits of the TzTz constituents. Addition of these extra substituents improved the solubility, on one hand, and, on the other hand, triggered the stacking tendency of the polymer resulting in a semicrystalline material. After purification by preparative SEC, the polymer showed a hole mobility of $1.0 \times 10^{-3} \text{cm}^2/(\text{V s})$ and organic solar cells constructed with a PCPDT-DTTzTz:PC$_{71}$BM active layer afforded a photovoltaic power conversion efficiency of 4.03% (without extensive optimization work). A noticeable increase in efficiency of more than 1% was obtained upon purification. The presented results clearly stress the crucial effects of the (alkyl) functionalization pattern and material purity on the photovoltaic performance of low bandgap polymer materials.

**EXPERIMENTAL SECTION**

**Materials and Methods.** NMR chemical shifts ($\delta$, in ppm) were determined relative to the residual CHCl$_3$ absorption (7.26 ppm) or the $^{13}$C resonance shift of CDCl$_3$ (77.16 ppm). Gas chromatography—mass spectrometry (GC-MS) analyses were carried out applying Chrompack CpsiS5CB or CpsiS8CB capillary columns. Molecular weights and molecular weight distributions were determined relative to polystyrene standards (Polymer Laboratories) by analytical size exclusion chromatography (SEC). Chromatograms were recorded on a Spectra Series P100 (Spectra Physics) equipped with two mixed-B columns (10 $\mu$m, 0.75 cm $\times$ 30 cm, Polymer Laboratories) and a refractive index detector (Shodex) at 40 °C. THF was used as the eluent at a flow rate of 1.0 mL/min. Preparative SEC was performed on JAIigel 2H and 2.5H columns attached to a LC system equipped with a UV detector (path 0.5 mm) and a switch for recycling and collecting the eluent (CHCl$_3$; flow rate 3.5 mL/min and injection volume 1.0 mL).

Solution UV−vis absorption measurements were performed with a scan rate of 600 nm/min in a continuous run from 200 to 800 nm. Thin film electrochemical measurements were performed with an Eco Chemie/Autolab PGSTAT 30 Potentiostat/Galvanostat using a conventional three-electrode cell under N$_2$ atmosphere (electrolyte: 0.1 M TBAPF$_6$ in anhydrous CH$_3$CN). For the measurements, a Ag/AgNO$_3$ reference electrode (0.01 M AgNO$_3$ and 0.1 M TBAPF$_6$ in anhydrous CH$_3$CN), a platinum counter electrode, and an indium tin oxide (ITO) coated glass substrate as working electrode were used. The polymers were deposited by drop-casting directly onto the ITO substrates. Cyclic voltammograms were recorded at 50 mV/s. From the onset potentials of the oxidation and reduction the position of the energy levels could be estimated. All potentials were referenced using a known standard, ferrocene/ferrocenium, which in CH$_3$CN solution is estimated to have an oxidation potential of $\sim$4.98 eV vs vacuum. DSC measurements were performed at 20 K/min in aluminum crucibles on a TA Instruments Q2000 Tzero DSC equipped with a refrigerated cooling system (RCS), using nitrogen (50 mL/min) as purge gas. TGA experiments were performed at 50 K/min in platinum crucibles on a TA Instruments Q5000 TGA using nitrogen (50 mL/min) as purge gas. The XRD measurements were performed with a Bruker D8 discover diffractometer under θ-2θ conditions. The system worked in parafocusing geometry using a Gobel mirror (line focus, mainly CuKα and CuKα2 rays). The X-rays were detected by a 1D detector.

Polymer solar cells were fabricated by spin-coating a PCPDT-DTTzTz:PC$_{71}$BM (Solene) blend in a 1:3 w/w ratio, sandwiched between a transparent anode and an evaporated metal cathode. The transparent anode was an ITO covered glass substrate which was coated with a 30 nm poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonic acid) PEDOT/PSS (CLEVIOS P VP.A1 4083) layer applied by spin-coating. The ITO glass substrate was cleaned by ultrasonification (sequentially) in soap solution, deionized water, acetone, and isopropanol. The cathode, a bilayer of 50 nm Ca and 100 nm Ag, was thermally evaporated. PCPDT-DTTzTz and PC$_{71}$BM (1:3 w/w ratio) were dissolved together in chlorobenzene to give an overall 40 mg/mL solution, which was stirred overnight at 80 °C inside a glovebox. Solar cell efficiencies were characterized under simulated 100 mW/cm$^2$ AM 1.5 G irradiation from a Xe arc lamp with an AM 1.5 global filter. Topography of the solar cells was studied by AFM, using a Picoscan PicoSPM LE scanning probe in tapping mode. The active layer morphology was studied with TEM (FEI Tecnai Spirit using an accelerating voltage of 120 kV).

Transistors were fabricated using heavily doped n-type Si wafers as bottom gate electrodes with a 200 nm thermally oxidized SiO$_2$ layer at the bottom gate dielectric. Au source and drain electrodes were defined by photolithography on a 2 nm Ti adhesion layer. The SiO$_2$ layer was passivated with hexamethyldisilazane prior to semiconductor deposition. The semiconducting active layer (30 nm) was spin-coated from a 0.5 wt % polymer solution in chlorobenzene. Before measurements, the substrates were annealed in vacuum at 100 °C. The measured transistors had a channel width (W) of 2500 $\mu$m and a channel length (L) of 10 $\mu$m. Electrical characterization was carried out in vacuum with an Agilent 4155C semiconductor parameter analyzer. Transistor performance was mainly evaluated by the thin film mobility ($\mu$) extracted in the linear regime and by the threshold voltage ($V_{th}$).

**Synthesis.** Unless stated otherwise, all reagents and chemicals were obtained from commercial sources and used without further purification. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was purchased from Acros Organics. THF was dried by distillation from Na/benzophenone. + (2‘-Ethylhexyl)-4-ocetyl-4H-cyclopenta[2,1-b:3,4-b’]dithiophene and 2,5-bis[(5′-bromo-3′-hexylthiophene-2′-yl)thiazolo[5,4-b]thiazole] (2) were synthesized according to previously reported procedures. Material identity and purity were confirmed by MS, 1H and 13C NMR.

![Figure 6](https://example.com/figure6.png) 

*Figure 6.* (a) Output curves for various gate biases. The gate bias was changed in 10 V steps from 0 V to $\sim$40 V. (b) Linear and saturated transfer characteristics of a PCPDT-DTTzTz transistor. The channel length and width were 10 and 2500 $\mu$m, respectively. The extracted mobilities were around $1.0 \times 10^{-3} \text{cm}^2/(\text{V s})$. 

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mmol) in DMF (50 mL) was added dropwise to a solution of 4-(2'-ethylhexyl)-4-ocyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (1.00 g, 2.5 mmol) in DMF (65 mL), after which the mixture was stirred overnight at rt. Subsequently, the mixture was purged onto ice and extracted with diethyl ether (3 × 100 mL). The combined organic layers were washed with NaHCO₃ (sat) and brine, dried over MgSO₄, and concentrated by evaporation to preparative size exclusion chromatograms indicating polymer aggregation, and ¹H and ¹³C NMR spectra of the CPDT and TzTz precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

**ASSOCIATED CONTENT**

2 Supporting Information

TGA curve and cyclic voltammogram of PCPDT-DTTrz, preparative size exclusion chromatograms indicating polymer aggregation, and ¹H and ¹³C NMR spectra of the CPDT and TzTz precursors. 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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