

## Photovoltaic performances of narrow bandgap copolymer derivatives based on 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene units

Dirk Vanderzande,<sup>1,2</sup> Sarah Van Mierloo,<sup>1</sup> Lidia Marin,<sup>1</sup> Pieter Verstappen,<sup>1</sup> Laurence Lutsen<sup>2</sup> and Wouter Maes<sup>1</sup>

<sup>1</sup> Hasselt University, Institute for Materials Research (IMO-IMOMEC), Wetenschapspark 1, B-3590 Diepenbeek, Belgium

<sup>2</sup> IMEC vzw, Kapeldreef 75, B-3001 Leuven, Belgium

### Introduction

Organic (polymer) solar cells (OSC's) offer great opportunities as renewable energy sources, as they combine some unique features such as low cost large-area fabrication, light weight, solution processability, (semi)transparency and flexibility.<sup>1</sup> To date, bulk heterojunction (BHJ) OSC's based on regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub> butyric acid methyl ester (PC<sub>61</sub>BM) as active layer donor and acceptor materials, respectively, have achieved power conversion efficiencies (PCE's) of 4–5%.<sup>1,2</sup> One of the main problems associated with the P3HT:PC<sub>61</sub>BM 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.<sup>1</sup> Incorporating alternating electron rich and electron deficient subunits within one polymer structure produces a significant decrease in the bandgap due to intramolecular charge transfer.

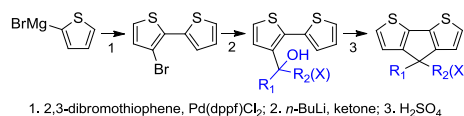
During recent years, 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) has emerged as an attractive heterocyclic system for organic photovoltaics (OPV) with good electron-donating properties, a rigid coplanar structure favoring  $\pi$ - $\pi$  intermolecular interactions, and the possibility of side-chain manipulation to influence solubility (and processability).<sup>3</sup> On the other hand, electron deficient systems such as 2,1,3-benzothiadiazoles (BT),<sup>1,3</sup> thiazolo[5,4-*d*]thiazoles (TzTz),<sup>4</sup> and quinoxalines (Qx)<sup>5</sup> have been introduced as interesting building blocks for integration in OPV devices due to their strong electron-withdrawing properties, high oxidative stability and straightforward synthesis. In this paper, CPDT has been combined with each of these electron poor systems in donor-acceptor alternating copolymers and blends of the resulting donor polymers with PC<sub>71</sub>BM were investigated as active layers in bulk heterojunction OSC's.

### Results and Discussion

To date, all high-performance CPDT-based low bandgap copolymers are synthesized from symmetrically dialkylated (either branched or linear) CPDT building blocks.<sup>3</sup> As it is nowadays generally accepted that the shape and size of the solubilizing alkyl side chains have a crucial effect on the photovoltaic performances of blends of polymers with fullerenes - affecting stacking properties (with an effect on crystallinity and hole mobility), morphology and miscibility - it was aimed to develop a novel synthetic protocol for CPDT derivatives allowing flexible introduction of different side chains.

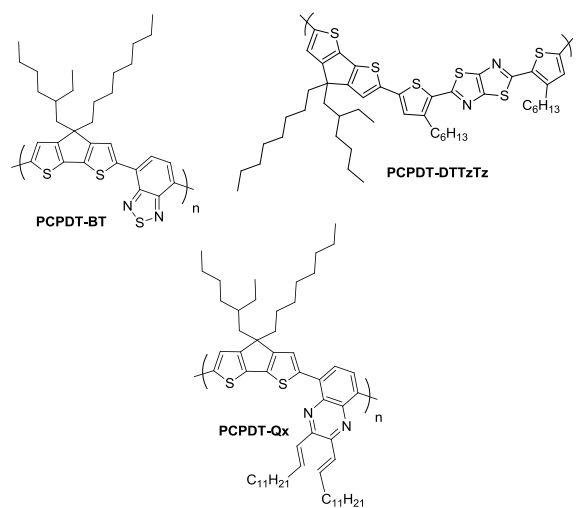
**Synthesis and Characterization.** A convenient and efficient three-step route toward both symmetrically and asymmetrically functionalized CPDT's has recently been developed within our group (Scheme 1).<sup>6</sup> Using this method a broad collection of functionalized bridged bithiophenes can smoothly be accessed. Starting from 3-bromo-2,2'-bithiophene, prepared by Kumada coupling of 2-thienylmagnesium bromide with 2,3-dibromothiophene under

Pd(dppf)Cl<sub>2</sub> catalysis, lithiation and subsequent reaction with dialkyl ketones afforded (a)symmetrically dialkylated tertiary alcohol derivatives. By means of final Friedel-Crafts dehydration cyclization in sulfuric acid medium, these derivatives were converted to 4,4-dialkyl-CPDT's.



**Scheme 1.** Three-step synthetic protocol toward asymmetrically substituted 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophenes.

For the first evaluations in OSC's, one particular CPDT derivative with a branched and a linear alkyl side chain was chosen, *in casu* the 4-(2-ethylhexyl)-4-octyl-CPDT. As the most performant CPDT-based copolymer to date is composed of alternating 4,4-bis(2-ethylhexyl)-CPDT and 2,1,3-benzothiadiazole units, affording 5.5% PCE,<sup>3b</sup> we first synthesized the analogous **PCPDT-BT** material. The dibrominated CPDT precursor was combined in a Suzuki polymerization reaction with the BT-bis(boronate) (Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, Aliquat, toluene, 80 °C for 3 days), affording a **PCPDT-BT** polymer in 80% yield after successive Soxhlet extractions and precipitation from MeOH (Figure 1).



**Figure 1.** Overview of the synthesized polymers: **PCPDT-BT**, **PCPDT-DTTzTz** and **PCPDT-Qx**.

Toward the second polymer material, the CPDT-bis(boronate) was prepared and combined with a dibrominated dithienyl-TzTz precursor<sup>7</sup> under similar Suzuki polycondensation conditions, affording a **PCPDT-DTTzTz** material in 64% yield after a similar work-up (Figure 1). For the electron deficient quinoxaline building block, a monomer with an extended absorption window was prepared by expanding the conjugated system in the vertical direction. Toward the desired **PCPDT-Qx** copolymer (Figure 1), the dibrominated quinoxaline was combined with the bis(trimethylstannyl)-CPDT analogue in a Stille polycondensation reaction.

**BHJ Organic Solar Cells.** After blending the polymers with PC<sub>71</sub>BM as an electron acceptor, BHJ OSC's were fabricated and the photovoltaic properties of the devices were investigated. Preliminary non-optimized device results are presented in Table 1.

**Table 1. PCE's for the PCPDT-X Copolymers.**

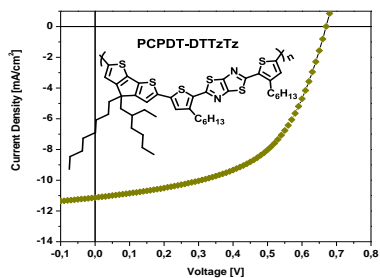
Polymer	$M_n$	PDI	$V_{oc}$	$J_{sc}$	FF	PCE
PCPDT-BT	$1.3 \times 10^4$	3.3	0.64	7.44	0.38	1.81
PCPDT-DTTzTz <sup>a</sup>	$1.7 \times 10^4$	2.9	0.58	9.0	0.47	2.43
PCPDT-DTTzTz <sup>b</sup>	$1.4 \times 10^4$	2.4	0.67	11.13	0.54	4.03

<sup>a</sup> Unpurified polymer. <sup>b</sup> Polymer purified by preparative SEC.

When the **PCPDT-BT** polymer, as obtained after Soxhlet extraction and precipitation ( $M_n$   $1.3 \times 10^4$ , PDI 3.3), was blended with PC<sub>71</sub>BM in a 1:3 w/w ratio and the active layer was spin coated from *o*-dichlorobenzene (with the addition of 1,8-octanedithiol), the resulting solar cell device (ITO/PEDOT:PSS/active layer/Yb/Ag) showed a rather moderate performance with an open circuit voltage ( $V_{oc}$ ) of 0.64 V, a fill factor (FF) of 0.38, a short-circuit current density ( $J_{sc}$ ) of 7.44 mA/cm<sup>2</sup>, and a resulting PCE of 1.81% under air mass 1.5 global illumination conditions (AM 1.5G; 100 mW/cm<sup>2</sup>) (Table 1). Compared to the top **PCPDT-BT** performance,<sup>3b</sup> the  $J_{sc}$  and FF are not at the required level.

The **PCPDT-DTTzTz** copolymer, as obtained after Soxhlet extraction and precipitation ( $M_n$   $1.7 \times 10^4$ , PDI 2.9), was also blended with PC<sub>71</sub>BM in a 1:3 w/w ratio. The active layer was spin coated from chlorobenzene (without any additive) and the resulting solar cell (ITO/PEDOT:PSS:active layer:Ca-Ag) showed a slightly better performance with a  $V_{oc}$  of 0.58 V, a FF of 0.47, a  $J_{sc}$  of 9.0 mA/cm<sup>2</sup>, and a resulting PCE of 2.43% (Table 1).

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. The solar cell device, prepared in an identical way, obtained from a purified batch of the polymer ( $M_n$   $1.4 \times 10^4$ , PDI 2.4) showed a significant increase in PCE of 1.6% (to 4.03%) by noticeable improvement of all three parameters ( $V_{oc}$  0.67 V, FF 0.54,  $J_{sc}$  11.13 mA/cm<sup>2</sup>; Table 1). The thin-film transistor field-effect mobility, calculated in the linear regime, was found to be  $1.0 \times 10^{-3}$  cm<sup>2</sup>/Vs, one order of magnitude higher than reported values in literature for different TzTz-based copolymers,<sup>4a</sup> and hence in good agreement with the photovoltaic properties. The **PCPDT-DTTzTz** polymer showed semi-crystalline behavior, as evidenced by DSC and XRD experiments.



**Figure 2.** *J-V* characteristics of the photovoltaic device fabricated from the purified **PCPDT-DTTzTz** batch.

The purified **PCPDT-DTTzTz** polymer formed homogeneous, well-distributed blend films with PC<sub>71</sub>BM, indicating good miscibility (or compatibility) with phase segregation on the nanometer scale (as evidenced by BF-TEM).

## Conclusions

We have successfully synthesized a series of novel low bandgap copolymers **PCPDT-X** ( $X = 2,1,3$ -benzothiadiazole, thiazolo[5,4-*d*]thiazole or quinoxaline), with asymmetrical alkyl substitution on the cyclopentadithiophene building block, by Suzuki and Stille polycondensation protocols. Preliminary investigations of these materials in organic solar cells have afforded a power conversion efficiency of 4.03% for the **PCPDT-DTTzTz**:PC<sub>71</sub>BM combination, without extensive optimization work (leaving room for further improvement). A noticeable increase in efficiency of 1.6% was obtained upon purification of the polymer by recycling SEC. 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.

**Acknowledgement.** The authors gratefully acknowledge the IWT for their financial support via the SBO-project 060843 "PolySpec". We also acknowledge the ONE-P project for the financial support from the European grant agreement n° 212311 related to the Hasselt-Eindhoven collaboration.

## References

- (a) Bundgaard, E.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 954. (b) Thompson, B. C.; Fréchet, J. M. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 58. (c) Boudreault, P. T.; Najari, A.; Leclerc, M. *Chem. Mater.* **2011**, *23*, 456.
- Dang, M. T.; Hirsch, L.; Wantz, G. *Adv. Mater.* **2011**, *23*, 3597.
- (a) Mühlbacher, D.; Scharber, M.; Morana, M.; Zhu, Z.; Waller, D.; Gaudiana, R.; Brabec, C. *Adv. Mater.* **2006**, *18*, 2884. (b) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497. (c) Bijleveld, J. C.; Shahid, M.; Gilot, J.; Wienk, M. M.; Janssen, R. A. J. *Adv. Funct. Mater.* **2009**, *19*, 3262. (d) Coffin, R. C.; Peet, J.; Rogers, J.; Bazan, G. C. *Nat. Chem.* **2009**, *1*, 657. (e) Tsao, H. N.; Cho, D. M.; Park, I.; Hansen, M. R.; Mavrinskiy, A.; Yoon, D. Y.; Graf, R.; Pisula, W.; Spies, H. W.; Müllen, K. *J. Am. Chem. Soc.* **2011**, *133*, 2605. (f) Manceau, M.; Bundgaard, E.; Carlé, J. E.; Hagemann, O.; Helgesen, M.; Søndergaard, R.; Jørgensen, M.; Krebs, F. C. *J. Mater. Chem.* **2011**, *21*, 4132.
- (a) Jung, I. H.; Yu, J.; Jeong, E.; Kim, J.; Kwon, S.; Kong, H.; Lee, K.; Woo, H. Y.; Shim, H.-K. *Chem. Eur. J.* **2010**, *16*, 3743. (b) Lee, S. K.; Cho, J. M.; Goo, Y.; Shin, W. S.; Lee, J.-C.; Lee, W.-H.; Kang, I.-N.; Shim, H.-K.; Moon, S.-J. *Chem. Commun.* **2011**, 1791. (c) Subramaniyan, S.; Xin, H.; Sunjoo Kim, F.; Shoaee, S.; Durrant, J. R.; Jenekhe, S. A. *Adv. Energy Mater.* **2011**, *1*, 854. (d) Zhang, M.; Sun, Y.; Guo, X.; Cui, C.; He, Y.; Li, Y. *Macromolecules* **2011**, *44*, 7625. (e) Helgesen, M.; Madsen, M. V.; Andreasen, B.; Tromholt, T.; Andreasen, J. W.; Krebs, F. C. *Polym. Chem.* **2011**, *2*, 2536.
- (a) Wang, E.; Hou, L.; Wang, Z.; Hellström, S.; Zhang, F.; Inganäs, O.; Andersson, M. R. *Adv. Mater.* **2010**, *22*, 5240. (b) Lee, S. K.; Lee, W.-H.; Cho, J. M.; Park, S. J.; Park, J.-U.; Shin, W. S.; Lee, J.-C.; Kang, I.-N.; Moon, S.-J. *Macromolecules* **2011**, *44*, 5994. (c) He, Z.; Zhang, C.; Xu, X.; Zhang, L.; Huang, L.; Chen, J.; Wu, H.; Cao, Y. *Adv. Mater.* **2011**, *23*, 3086. (d) Zhang, Y.; Zou, J.; Yip, H.-L.; Chen, K.-S.; Zeigler, D. F.; Sun, Y.; Jen, A. K.-Y. *Chem. Mater.* **2011**, *23*, 2289.
- Van Mierloo S.; Adriaensens, P.; Maes, W.; Lutsen, L.; Cleij, T. J.; Botek, E.; Champagne, B.; Vanderzande, D. J. *J. Org. Chem.* **2010**, *75*, 7202.
- Van Mierloo, S.; Chambon, S.; Boyukbayram, A. E.; Adriaensens, P.; Lutsen, L.; Cleij, T. J.; Vanderzande, D. *Magn. Reson. Chem.* **2010**, *48*, 362.