Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2016, **26**, 248–250

Mendeleev Communications

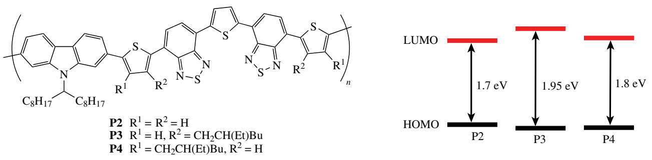
Design of highly soluble PCDTBTBT-type conjugated polymers for organic solar cells

Alexander V. Akkuratov,[a] Diana K. Susarova,[a] Olga A. Mukhacheva[a] and Pavel A. Troshin*[a,b]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 515 5420; e-mail: troshin2003@inbox.ru*
[b] *Skolkovo Institute of Science and Technology, 143025 Skolkovo, Moscow Region, Russian Federation*

DOI: 10.1016/j.mencom.2016.05.009

Two novel polymers comprising TBTBT units bearing alkyl side chains in different arrangements were synthesized and investigated as electron donor materials in organic solar cells. The presence of alkyl chains significantly improves the material solubility with simultaneous increase in the material band gap and causes minor improvement in the photovoltaic performance.



Conjugated polymers containing alternating electron donor (D) and electron acceptor (A) units are widely used as materials in organic electronic devices: solar cells, light emitting diodes and organic field effect transistors.[1] Conjugated polymer PCDTBT comprising carbazole, thiophene and benzothiadiazole units represents one of the most promising examples of the (–X–DAD)$_n$ family of polymers.[2] Power conversion efficiencies (PCE) of bulk heterojunction solar cells based on this material approach 6–7%.[3] In addition, PCDTBT (**P1**) (Figure 1) shows advanced stability under ambient conditions[4] and possesses a deep lying HOMO energy level providing high open-circuit voltages in the solar cells (V_{OC} > 800 mV).[5] Unfortunately, PCDTBT has a large band gap (~1.9 eV) which limits short-circuit current density and also efficiency of solar cells based on this material. A number of attempts to modify the chemical structure of PCDTBT did not allow one to improve its optoelectronic and photovoltaic characteristics.[7,8]

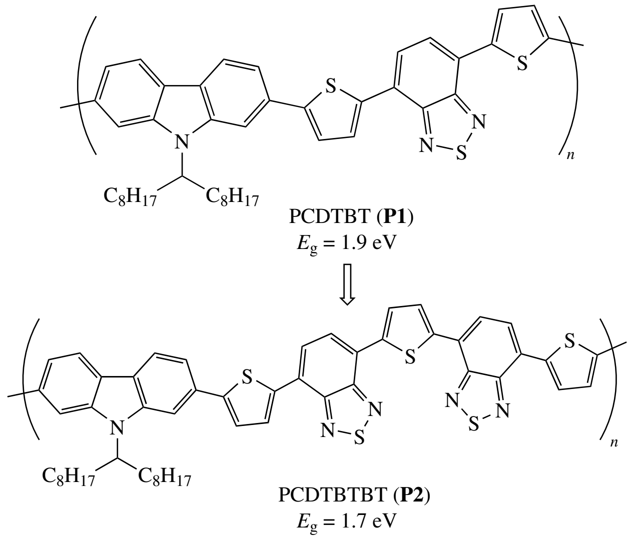


Figure 1 Molecular structures of polymers **P1** and **P2** comprising TBT and TBTBT fragments, respectively.

Recently we have reported an alternative design of promising conjugated polymers with improved optoelectronic properties comprising alternating oligomeric T′TBTBTT′ units [T – thiophene, T′ – 3-(2-ethylhexyl)thiophene, B – benzothiadiazole].[9] In particular, the band gap (E_{g}) of PCDTBT was reduced by 0.2 eV *via* replacement of TBT with extended T′TBTBTT′ fragments. PCE of solar cells based on the designed material exceeded 6% with a potential of further increase up to 10% due to the optimal HOMO/E_{g} combination.

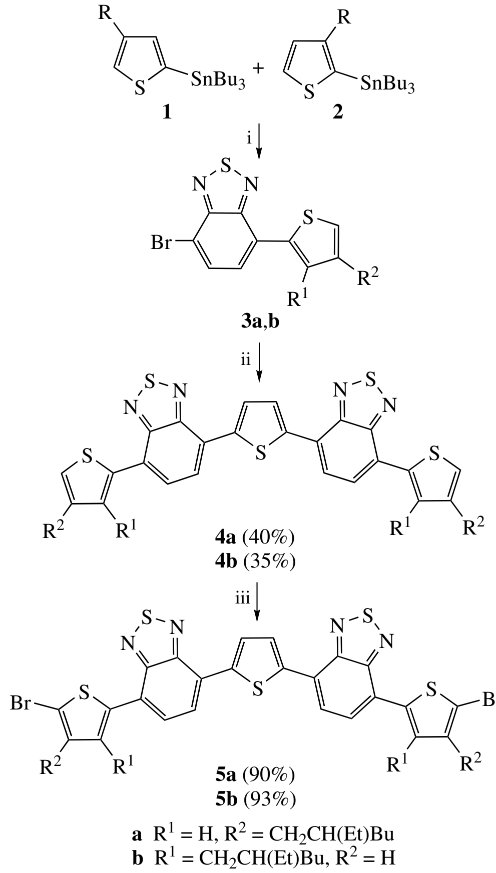
Polymer PCDTBTBT (**P2**) (Figure 1) is another promising material with a band gap E_{g} = 1.7 eV and HOMO energy of –5.53 eV leading to the theoretically attainable PCE of 9–10%.[9,10] Unfortunately, the solar cells based on polymer **P2** revealed low experimental efficiencies of ~1%. Poor photovoltaic characteristics are related to an extremely low solubility of polymer **P2** in organic solvents leading to its strong segregation from the fullerene component in the photoactive layer of the devices.

Herein, we prepared two highly soluble analogues of polymer **P2** and investigated their optoelectronic and photovoltaic properties. Introduction of alkylthiophenyl units instead of bare thiophene rings was proposed as a way to increase the solubility of polymer **P2** (Scheme 1).

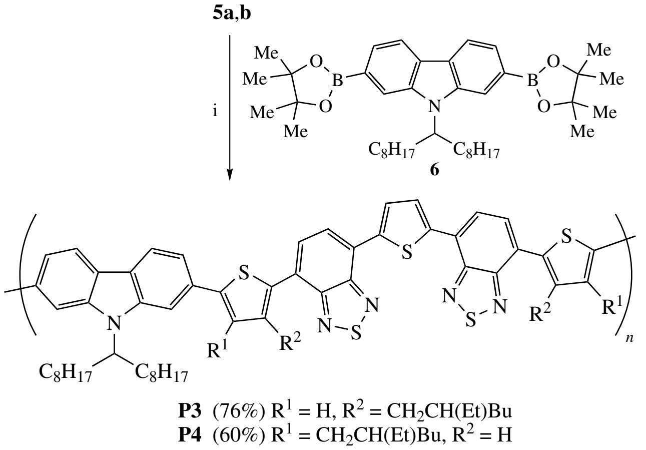
Compounds **3a**,**b** were obtained *in situ* using Stille cross-coupling reaction between 4,7-dibromo-2,1,3-benzothiadiazole and tributyl[4-(2-ethylhexyl)thiophen-2-yl]stannane **1** or tributyl[3-(2-ethylhexyl)thiophen-2-yl]stannane **2**, which were further converted to **4a**,**b** by coupling with 0.5 equiv. of 2,5-bis(trimethylstannyl)thiophene. Dibromination of **4a**,**b** with *N*-bromosuccinimide (NBS) in *o*-dichlorobenzene afforded the key monomers **5a**,**b**. Monomer **6** was prepared following the previously described procedure.[11]

The conjugated polymers **P3** and **P4** were synthesized using Suzuki polycondensation reaction between the monomers **5a**,**b** and the carbazole-based monomer **6** (Scheme 2).

Gel permeation chromatography was used to reveal the molecular weight characteristics of polymers **P3** (M_{w} = 95 000 g mol^{-1}, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 2.0) and **P4** (M_{w} = 36 000 g mol^{-1}, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.5). Both polymers showed high solubility in organic solvents in contrast



Scheme 1 *Reagents and conditions*: i, 4,7-dibromo-2,1,3-benzothiadiazole (1 equiv.), Pd(PPh_3)$_4$, toluene, reflux; ii, 2,5-bis(trimethylstannyl)thiophene, Pd(PPh_3)$_4$, toluene, reflux; iii, NBS, 1,2-dichlorobenzene, 50 °C.



Scheme 2 *Conditions*: i, Pd(PPh_3)$_4$, toluene, 2 M K_2CO_3, aliquat 336, reflux.

to the previously reported polymer **P2**. The absorption spectra of polymers **P2–P4** are compared in Figure 2.

The main absorption bands in the spectra of polymers **P3** (λ_{edge} = 614 nm) and **P4** (λ_{edge} = 675 nm) show rather strong hypsochromic shifts as compared to polymer **P2** (λ_{edge} = 730 nm). The optical band gaps of **P3** and **P4** estimated from the absorption spectra of their thin films (Figure S1, Online Supplementary Materials) are equal to 1.95 and 1.80 eV, respectively (Table 1).

The onsets of the oxidation waves of **P2–P4** were determined using cyclic voltammetry (CV) measurements (Figure 3).[12] The potentials were referenced *vs.* Fc$^+$/Fc couple. Assuming that the HOMO energy level of Fc is –5.10 eV, we estimated the HOMO and LUMO energies of these polymers (Table 1).

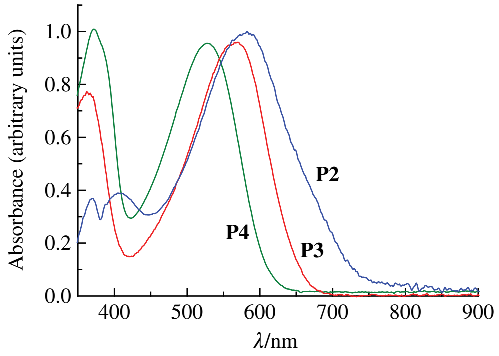


Figure 2 The absorption spectra of polymers **P2–P4** in *o*-dichlorobenzene.

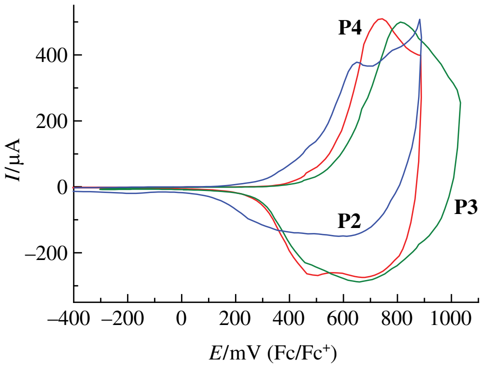


Figure 3 Cyclic voltammograms of thin films of **P2–P4** deposited on glassy carbon disc electrode.

The HOMO energies of **P3** and **P4** are considerably lower than that of **P2**. It is known that the open circuit voltage (V_{OC}) of bulk-heterojunction solar cells correlates with the energy gap between the LUMO of the electron acceptor fullerene derivative and HOMO of electron donor conjugated polymer.[13] Therefore, higher V_{OC} can be expected for solar cells based on **P3** and **P4** as compared to **P2**.

The bulk-heterojunction solar cells were fabricated using a standard device configuration: ITO / (PEDOT : PSS)/polymer : [60]PCBM / Ca / Ag. The procedure used for fabrication of such devices was reported previously.[14] Fullerene derivative [60]PCBM was used as a conventional electron acceptor material.[15] The current–voltage characteristics were measured using Keithley 2400 source/measurement unit under simulated AM1.5G 100 mW cm^{-2} solar irradiation. The obtained data are given in Table 2.

Unfortunately, the characteristics of the solar cells based on the designed polymers **P3**, **P4** were lower than expected. The maximum PCE of just 1.2% was obtained for **P4** / [60]PCBM system. It is notable that the devices based on polymer **P3** showed the highest V_{OC} of 800 mV. However, the short circuit current densities (J_{SC}) and fill factors (FF) remain low for all three polymers.

Table 1 Electrochemical and optical properties of PCDTBT and **P2–P4**.

Polymer	E^{ox}_{onset}/V *vs.* Fc/Fc$^+$ [a]	E_{HOMO}/eV[b]	E_{LUMO}/eV[c]	E^{opt}_g/eV[d]
PCDTBT	0.40	–5.50	–3.59	1.91
P2	0.45	–5.55	–3.85	1.70
P3	0.52	–5.62	–3.67	1.95
P4	0.51	–5.61	–3.81	1.80

[a] Estimated from CV data. [b] HOMO energies were estimated from onsets of the oxidation waves in cyclic voltammograms of thin polymer films. [c] LUMO energy was calculated as $E_{HOMO} + E^{opt}_g$. [d] Values are given for the solid-state absorption spectra.

Table 2 Parameters of solar cells based on the blends of **P2**–**P4** with [60]PCBM.

Polymer	V_{OC}/mV	J_{SC}/mA cm^{-2}	FF (%)	η (%)
P2	706	4.5	30	0.9
P3	800	3.3	33	0.9
P4	701	4.7	36	1.2

In conclusion, we have synthesized two conjugated polymers which represent soluble analogues of PCDTBTBT (**P2**). However, introduction of alkyl side chains into the structures of **P3** and **P4** negatively affected all their optoelectronic properties as compared to the non-solubilized polymer **P2**. The observed increase in the optical band gaps of **P3**, **P4** *vs.* **P2** seems to be related to the twisting of the polymer backbone due to steric hindrance effects induced by the bulky alkyl side chains. Some steric repulsion can be expected between the alkyl substituents and benzothiadiazole moiety of polymer **P3**. In the case of polymer **P4** it seems that some steric hindrance effects arise due to the overlap of alkyl chains attached to thiophene rings and alkyl substituents of neighbouring carbazole units. The twisting of the polymer backbone breaks the conjugation in the polymer chain, which damages optical, electronic and photovoltaic properties of these materials.

The revealed problem can be potentially solved by changing the positions of the alkyl substituents in the polymer backbone. In particular, the alkyl substituents located at the 5- and 6-positions of benzothiadiazole moieties should not cause steric hindrance and distortion of the planar structure of the main polymer chain. Another approach is to use branched long-chain (C_{25}–C_{45}) alkyl substituents attached to the carbazole moiety.

This work was supported by the Russian Foundation for Basic Research (grant nos. 14-03-31681 and 16-33-60174 mol-a-dk) and Research Program of the Russian Academy of Sciences (OHNM 03). We thank Dr. D. V. Novikov for assistance with the electrochemical measurements.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.05.009.

References

1 (*a*) X. Zhao and X. Zhan, *Chem. Soc. Rev.*, 2011, **40**, 3728; (*b*) C. J. Brabec, N. S. Sariciftci and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 15; (*c*) M. Morana, P. Koers, C. Waldauf, M. Koppe, D. Muehlbacher, P. Denk, M. Scharber, D. Waller and C. Brabec, *Adv. Funct. Mater.*, 2007, **17**, 3274; (*d*) H. E. Katz, *Chem. Mater.*, 2004, **16**, 4748.

2 (*a*) S. Beaupre and M. Leclerc, *J. Mater. Chem. A*, 2013, **1**, 11097; (*b*) N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2008, **130**, 732.

3 (*a*) Y. Sun, C. J. Takacs, S. R. Cowan, J. H. Seo, X. Gong, A. Roy and A. J. Heeger, *Adv. Mater.*, 2011, **23**, 2226; (*b*) T.-Y. Chu, S. Alem, S.-W. Tsang, S.-C. Tse and S. Wakim, *Appl. Phys. Lett.*, 2011, **98**, 253301.

4 C. H. Peters, I. T. Sachs-Quintana, J. P. Kastrop, S. Beaupré, M. Leclerc and M. D. McGehee, *Adv. Energy Mater.*, 2011, **1**, 491.

5 (*a*) H. Zhou, L. Yang and W. You, *Macromolecules*, 2012, **45**, 607; (*b*) R. S. Kularatne, H. D. Magurudeniya, P. Sista, M. C. Biewer and M. C. Stefan, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 743.

6 D. H. Wang, A. K. K. Kyaw and J. H. Park, *ChemSusChem*, 2015, **8**, 331.

7 W. Zhao, W. Cai, R. Xu, W. Yang, X. Gong, H. Wu and Y. Cao, *Polymer*, 2010, **51**, 3196.

8 E. Zhou, M. Nakamura, T. Nishizawa, Y. Zhang, Q. Wei, K. Tajima, C. Yang and K. Hashimoto, *Macromolecules*, 2008, **41**, 8302.

9 A. V. Akkuratov, D. K. Susarova, O. V. Kozlov, A. V. Chernyak, Yu. L. Moskvin, L. A. Frolova, M. S. Pshenichnikov and P. A. Troshin, *Macromolecules*, 2015, **48**, 2013.

10 T. Ameri, G. Dennler, C. Lungenschmied and C. J. Brabec, *Energy Environ. Sci.*, 2009, **2**, 347.

11 N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.*, 2007, **19**, 2295.

12 C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367.

13 C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispens, L. Sanchez and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 374.

14 I. E. Kuznetsov, D. K. Susarova, L. N. Inasaridze, M. V. Klyuev and P. A. Troshin, *Mendeleev Commun.*, 2015, **25**, 277.

15 J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao and C. L. Wilkins, *J. Org. Chem.*, 1995, **60**, 532.

Received: 19th October 2015; Com. 15/4755