



Statistical carbazole-fluorene-TTBTBTT copolymers as promising electron donor materials for organic solar cells

Journal:	<i>ChemComm</i>
Manuscript ID:	CC-COM-01-2015-000678.R1
Article Type:	Communication
Date Submitted by the Author:	12-Mar-2015
Complete List of Authors:	Kuznetsov, Iliya; IPCP RAS, ; Ivanovo State University, Chemistry and Biology Akkuratov, Alexander; IPCP RAS, Susarova, Diana; IPCP RAS, Anokhin, Denis; IPCP RAS, Moskvin, Yuriy; Institute for Energy Problems of Chemical Physics of Russian Academy of Science (Branch), Klyuev, Mikhail; Ivanovo State University, Chemistry and Biology Peregudov, Alexander; INEOS RAS, Troshin, Pavel; Institute for Problems of Chemical Physics of Russian Academy of Sciences,

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Statistical carbazole-fluorene-TTBTBTT terpolymers as promising electron donor materials for organic solar cells

Iliya E. Kuznetsov,^{a,b} Alexander V. Akkuratov,^a Diana K. Susarova,^a Denis V. Anokhin,^c Yuriy L. Moskvina,^d Mikhail V. Klyuev,^b Alexander S. Peregudov,^e and Pavel A. Troshin^{a*}

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

We report the application of a statistical Suzuki-Miyaura polycondensation reaction for synthesis of a family of carbazole-fluorene-TTBTBTT terpolymers with tailored physical and optoelectronic properties. Organic bulk heterojunction solar cells based on the designed materials with optimal fluorene to carbazole ratios yielded reproducible power conversion efficiencies of 6.5-6.7%.

Organic solar cells based on conjugated polymers currently demonstrate high power conversion efficiencies approaching 8-10% for the best material combinations.¹ Unfortunately, the most efficient electron donor materials undergo rapid photochemical degradation which dramatically affects the operational stability of the devices.² Additionally, long operation lifetimes have been predicted for some less efficient conjugated polymers possessing very robust chemical structures. In particular, a lifetime exceeding 7 years was estimated for solar cells based on [70]PCBM/PCDTBT blends.³

Recently we have pursued the design of PCDTBT-like polymers in order to achieve improved photovoltaic performances in combination with the enhanced stability. The first developed carbazole-TTBTBTT copolymer **P1** (Fig. 1) demonstrated promising solar cell efficiencies of 5-6% with a potential to increase further up to 8-9%.⁴ Notably, this material with a band gap (E_g) of 1.65 eV showed a comparable operational stability in devices when compared to the reference wider band gap polymer PCDTBT ($E_g=1.9$ eV). However, further development of the TTBTBTT polymers is required in order to make these materials competitive not only with regards to their stability, but also in terms of their photovoltaic performance.

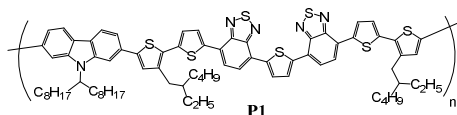
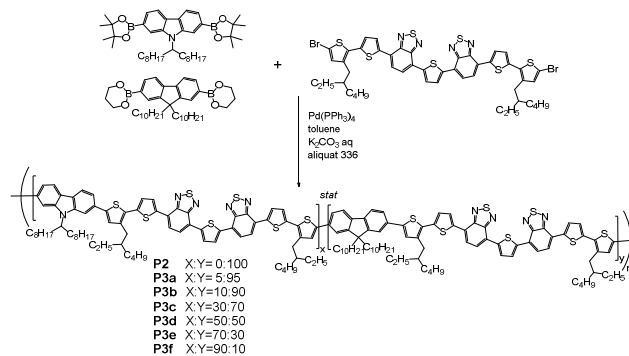


Figure 1. Molecular structure of **P1**

A number of recent reports have highlighted statistical copolymers exhibiting appreciably high power conversion efficiencies in organic solar cells.⁵ It is also known that fluorene-thiophene-benzothiadiazole copolymers (e.g. F8TBT

or F10TBT) demonstrate good operational stability and give higher open circuit voltages (V_{OC}) in photovoltaic cells than corresponding carbazole-based analogs.⁶

Here we report the design and investigation of novel fluorene-TTBTBTT architectures which can be considered as promising electron donor materials for efficient organic solar cells. A family of fluorene-based copolymers and terpolymers possessing regioregular (**P2**) and regiorandom (**P3a-f**) structures was prepared using Suzuki-Miyaura polycondensation of fluorene, TTBTBTT (T-thiophene, B-benzothiadiazole), and carbazole-based monomers (experimental details are given in Electronic supplementary information, ESI). The molar ratio between the fluorene and carbazole units in the statistical terpolymers **P3a-f** was varied from 10:90 to 95:5 (Scheme 1).



Scheme 1. Synthesis of statistical copolymers

All conjugated polymers were obtained with high molecular weights and reasonable polydispersities (Table 1). These materials were characterized using optical spectroscopy and cyclic voltammetry (CV). It was observed that variation of the fluorene-carbazole ratio in the molecular structures of the polymers results in noticeable changes in their optical properties (Fig S1, ESI). In particular, introduction of just 10% of the carbazole unit in **P3b** leads to a bathochromic shift of the absorption band maximum (619 nm) as compared to the fluorene-based polymer **P2** (603 nm). The polymer **P3d** with an equal fluorene-to-carbazole ratio shows a broad absorption band which can be fitted well by superposition of the **P1** and **P2** absorptions taken with the same contributions. At the same time, onset potentials of the oxidation waves in cyclic voltammograms of copolymers **P3a-f** are found between that

of **P1** and **P2** (Fig S2, ESI). The optoelectronic properties of the statistical terpolymers **P3a-f** are compared with the properties of the “parent” regular copolymers **P1** and **P2** in Table 1. It can be seen from this data that all investigated materials have virtually identical optical band gaps of 1.65 eV as defined by the edge positions of their absorption bands at long wavelengths. The HOMO energies of the statistical terpolymers decrease in parallel with the increasing content of the fluorene units in the main chain. It is known that lowering the HOMO energy of the polymer leads to an increase in the open circuit voltage of organic solar cells based on this material.⁷ Therefore, we can expect that conjugated polymers **P2** and **P3a-d** with high fluorene loading will show improved characteristics in photovoltaic cells.

Table 1. Optoelectronic properties of conjugated polymers

Polymer	M _w g/mol	M _w /M _n	HOMO, ¹ eV	LUMO, ² eV	E _g , ³ eV	μ _h , ⁴ cm ² V ⁻¹ s ⁻¹
P2	175000	5.3	-5.62	-3.95	1.66	1.8×10 ⁻⁴
P3a	115000	5.6	-5.57	-3.91	1.65	4.1×10 ⁻⁵
P3b	231200	3.5	-5.56	-3.89	1.65	8.1×10 ⁻⁵
P3c	199300	4.0	-5.56	-3.89	1.66	1.1×10 ⁻⁴
P3d	199200	2.9	-5.55	-3.85	1.65	4.8×10 ⁻⁵
P3e	153200	3.6	-5.52	-3.85	1.65	5.5×10 ⁻⁵
P3f	201200	4.3	-5.50	-3.84	1.65	8.4×10 ⁻⁴
P1	191000	5.0	-5.47	-3.79	1.65	2.8×10 ⁻⁴

¹ HOMO energies were estimated from onsets of the oxidation waves in cyclic voltammograms of thin polymer films (see ESI, Fig. S2) following ref. 8. ² LUMO energy was calculated as E(HOMO)+E_g. ³ E_g was determined from the onset of the absorption edge at long wavelengths. ⁴ SCLS mobility was determined in hole-only devices (see ESI, Fig. S3)

The space charge limited current (SCLC) mobilities estimated in hole-only devices (see ESI) were found to be rather different for the investigated materials. In general, the statistical terpolymers showed lower charge carrier mobilities as compared to the regioregular **P1** and **P2** copolymers which might be a consequence of their more disordered molecular structures. The only exception was terpolymer **P3f**, with a low fluorene loading, which demonstrated superior charge transport characteristics (Table 1).

We investigated thin films of polymers **P1**, **P2**, and **P3a-f** using grazing incident wide angle X-ray scattering (GIWAXS). In addition to the broad amorphous halo, all of the curves show the presence of intense peaks in the small-angle region. Such patterns indicate the formation of poorly ordered lamellar film morphology (Fig. S4).

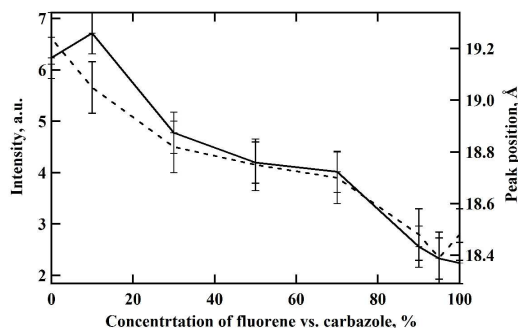


Figure 2. The dependence of the relative intensity (solid line) and position (dashed line) of lamellar peak on the content of carbazole vs. fluorene units in the polymer backbone

The degree of ordering of the polymer chains in the films depends strongly on the ratio between the fluorene and carbazole units in the molecular structure of the material. The highest scattering intensities were observed for polymers **P1** and **P3f** thus proving their superior ordering in the films (Fig. 2). The peak position also depended on the carbazole-fluorene ratio. The smallest interlayer distance was observed for **P1** due to a better ordering of this material in thin films as compared to the polymers **P2** and **P3a-b**.

The designed polymers **P3a-f** were investigated as electron donor materials in organic bulk heterojunction solar cells using [70]PCBM and [60]PCBM (Table S2, ESI) as an electron acceptor counterpart. We used the standard device geometry ITO/PEDOT:PSS/fullerene-polymer blend/Ca/Ag (see device fabrication procedure in ESI). The current-voltage (J-V) characteristics and EQE spectra of the devices comprising regioregular polymers **P1**, **P2** and the best statistical terpolymer **P3b** are presented in Fig. 3.

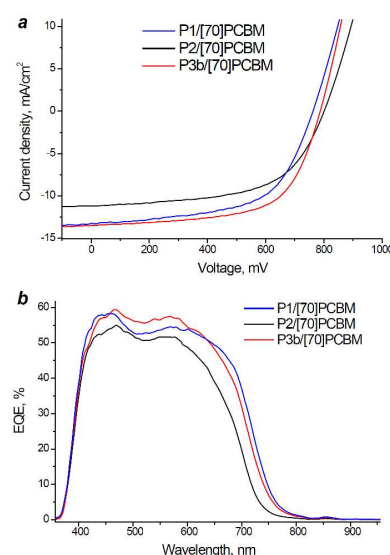


Figure 3. J-V plots (a) and EQE spectra (b) for organic solar cells based on the blends of polymers **P1**, **P2** and **P3b** with [70]PCBM

It can be seen from the figure that solar cells based on the **P1**/[70]PCBM blends give reasonably high current densities, while the open circuit voltage stays near 750 mV. On the contrary, the **P2**/[70]PCBM system gives open circuit voltages exceeding 800 mV, but the J_{SC} is much lower compared to the **P1**-based cells. It is rather remarkable that the statistical terpolymer **P3b** combines the advantages of the “parent” copolymers and shows simultaneously high current densities and open circuit voltages resulting in an overall solar light power conversion efficiency of 6.7%. It should be emphasized that the presence of just 10% of the carbazole unit in **P3b** significantly improves its optical and photovoltaic properties in comparison to **P2** as it is illustrated by the EQE spectra shown in Fig. 3b. Apparently, the carbazole unit is crucial for harvesting the low energy photons in the 730-770 nm range.

The parameters of the photovoltaic cells based on the blends of all of the investigated polymers with [70]PCBM are listed in the Table 2. The J-V plots and EQE spectra for all systems are given in Fig. S5 (ESI). The influence of the molecular

composition of the polymer-based materials on the open circuit voltage and power conversion efficiency of the devices is illustrated by Fig. 4.

Table 2. Parameters of the solar cells based on the blends of **P1**, **P2**, **P3a-f** and [70]PCBM*

Polymer	Ratio/additive*	V _{OC} , mV	J _{SC} , mA/cm ²	FF, %	η, %
P1	1:2, 0.6% DIO	757	13.3	58	6.0
P2	1:3.5, 0.6% DIO	801	11.2	58	5.2
P3a	1:2, 0.3% DIO	793	13.6	58	6.2
P3b	1:2.5, 0.3% DIO	788	13.5	63	6.7
P3c	1:2.5, 0.6% DIO	786	12.2	58	5.6
P3d	1:2.5, 0.6% DIO	779	11.8	60	5.6
P3e	1:1.5, 0.6% DIO	752	12.1	56	5.1
P3f	1:2, 0.6% DIO	715	12.4	55	4.9

* - Optimal polymer to [70]PCBM w/w ratio is given, DIO corresponds to the 1,8-diiodooctane additive

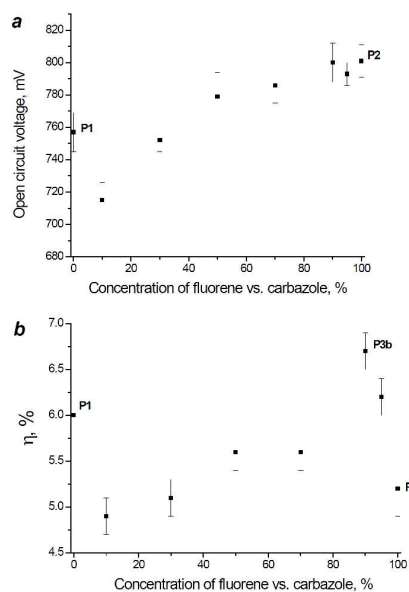


Figure 4. The open circuit voltage (a) and solar cell power conversion efficiency (b) as functions of the molecular composition of conjugated polymers blended with [70]PCBM

The open circuit voltage increases as the content of the fluorene units in the polymer chain increases. This result correlates well with the electrochemistry data and the estimated HOMO energies of the polymers given in Table 1 above. The solar cell power conversion efficiency reaches the maximum at a fluorene-to-carbazole ratio of 90:10. Most probably, this composition of the polymer **P3b** provides the best results due to the balanced optical (narrow band gap) and electronic (deep-lying HOMO) properties as well as obtaining an optimal blend morphology (see AFM images in Fig. S6, ESI).

In conclusion, we have shown that the optoelectronic properties of conjugated polymers can be tailored successfully using statistical polymerization of certain building blocks used in appropriate amounts. This approach has a high potential for being used to improve the photovoltaic performances of many existing electron donor materials.

This work was supported by the Russian Science Foundation (grant No. 14-13-01031). We gratefully acknowledge Dr. D.

V. Novikov and Dr. A. V. Chernyak for carrying out CV measurements and NMR characterization of some compounds, respectively.

Notes and references

- ³⁵ *IPCP RAS, Semenov Prospect 1, Chernogolovka, Moscow region, 141432, Russia. Tel: +7 496522 1418; E-mail: troshin2003@inbox.ru*
- ^b *Ivanovo State University, Ermaka, 39, Ivanovo*
- ^c *Moscow State University, Faculty of Fundamental Physical and Chemical Engineering, GSP-1, Leninskie Gory, Moscow, 119991, Russia*
- ⁴⁰ ^d *The Branch of Talrose Institute for Energy Problems of Chemical Physics RAS, Chernogolovka, Moscow region, 141432, Russia.*
- ^e *INEOS RAS, Vavylova St. 28, B-334, Moscow, 119991, Russia*
- [†] Electronic Supplementary Information (ESI) available: absorption spectra, cyclic voltammograms, J^{1/2}-V plots for hole-only devices, J-V curves and EQE spectra for solar cells, AFM images. See DOI: 10.1039/b000000x/
- 1 B. Zhao, Z. He, X. Cheng, D. Qin, M. Yun, M. Wang, X. Huang, J. Wu, H. Wu and Y. Cao, *J. Mater. Chem. C.*, 2014, 2, 5077; M. Zhang, Y. Gu, X. Guo, F. Liu, S. Zhang, L. Huo, T. Russell and J. Hou, *Adv. Mater.*, 2013, 25, 4944; C. Cabanetos, A. Labban, J. Bartelt, J. Douglas, W. Mateker, J. Frechet, M. McGehee and P. Beaujuge, *J. Am. Chem. Soc.*, 2013, 135, 4656; Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade, H. Yan, *Nat. Commun.* 2014, 5, 5293
- 2 M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.* 2012, 24, 580; Y. W. Soon, H. Cho, J. Low, H. Bronstein, I. McCulloch, J. R. Durrant *Chem. Commun.* 2013, 49, 1291; E. A.A. Arbab, B. Taleatu, G. T. Mola, *J. Mod. Opt.* 2014, 61, 1749; L. A. Frolova, N. P. Piven, D. K. Susarova, A. V. Akkuratov, S. D. Babenko, P.A. Troshin, *Chem. Comm.*, 2015, 51, DOI: 10.1039/C4CC08146C
- 3 C. H. Peters, I. T. S.-Quintana, J. P. Kastrop, S. Beauprer, M. Leclerc, M. D. McGehee, *Adv. Energy Mater.*, 2011, 1, 491
- 4 A V. Akkuratov, D. K. Susarova, D. V. Novikov, D. V. Anokhin, Y. L. Moskvina, A. V. Chernyak, F. A. Prudnov, S. D. Babenko, and P. A. Troshin, *J. Mater. Chem. C.* 2015, 3, 1497; A. V. Akkuratov, D. K. Susarova, O. Kozlov, D. V. Novikov, Y. L. Moskvina, L. A. Frolova, A. V. Chernyak, M. S. Pshenichnikov, P. A. Troshin, *submitted*
- 5 S. J. Park, J. M. Cho, W.-B. Byun, J.-C. Lee, W. S. Shin, I.-N. Kang, S.-J. Moon, S. K. Lee, *J. Polym. Sci A: Polym. Chem.* 2011, 49, 4416; B. Xu, S. Noh, B. C. Thompson, *Macromolecules* 2014, 47, 5029; D. C. Lim, K.-D. Kim, S.-Y. Park, E. M. Hong, H. O. Seo, J. H. Lim, K. H. Lee, Y. Jeong, C. Song, E. Lee, Y. D. Kim, S. Cho, *Energy Environ. Sci.* 2012, 5, 9803; L. Fang, Y. Zhou, Y.-X. Yao, Y. Diao, W.-Y. Lee, A. L. Appleton, R. Allen, J. Reinspach, S. C. B. Mannsfeld, Z. Bao, *Chem. Mater.* 2013, 25, 4874; J. W. Jung, F. Liu, T. P. Russell, W. H. Jo, *Energy Environ. Sci.*, 2013, 6, 3301; T. E. Kang, H.-H. Cho, H. j. Kim, W. Lee, H. Kang, B. J. Kim, *Macromolecules* 2013, 46, 6806; P. P. Khlyabich, B. Burkhart, C. F. Ng, B. C. Thompson, *Macromolecules* 2011, 44, 5079; D. Kotowski, S. Luzzati, G. Bianchi, A. Calabrese, A. Pellegrino, R. Po, G. Schimperna, A. Tacca, *J. Mater. Chem. A*, 2013, 1, 10736; J.-M. Jiang, H.-C. Chen, H.-K. Lin, C.-M. Yu, S.-C. Lan, C.-M. Liu, K.-H. Wei, *Polym. Chem.*, 2013, 4, 5321; J. Li, K.-H. Ong, S.-L. Lim, G.-M. Ng, H.-S. Tan, Z.-K. Chen, *Chem. Commun.*, 2011, 47, 9480; Y.-H. Chao, J.-F. Jheng, J.-S. Wu, K.-Y. Wu, H.-H. Peng, M.-C. Tsai, C.-L. Wang, Y.-N. Hsiao, C.-L. Wang, C.-Y. Lin, C.-S. Hsu, *Adv. Mater.* 2014, 26, 5205.
- 6 F. Zhang, K. G. Jespersen, C. Björström, M. Svensson, M. R. Andersson, V. Sundström, K. Magnusson, E. Moons, A. Yartsev, O. Inganäs, *Adv. Funct. Mater.* 2006, 16, 667; L. H. Slooff, S. C. Veenstra, J. M. Kroon, D. J. D. Moet, J. Sweelssen and M. M. Koetse, *Appl. Phys. Lett.* 2007, 90, 143506
- 7 C. J. Brabec, A. Cravino, D. Meissner, N. S. Sariciftci, T. Fromherz, M. T. Rispen, L. Sanchez, J. C. Hummelen, *Adv. Funct. Mater.* 2001, 11, 374
- 8 C.M. Cardona, Wei Li, A.E. Kaifer, D. Stockdale, G.C. Bazan, *Adv. Mater.* 2011, 23, 2367