Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2015, **25**, 277–279

Mendeleev
Communications

Synthesis of statistical carbazole–fluorene–thiophene–benzothiadiazole copolymers and their investigation in organic solar cells

Iliya E. Kuznetsov,[a,b] Diana K. Susarova,[a] Liana N. Inasaridze,[a] Mikhail V. Klyuev[b] and Pavel A. Troshin*[a]

[a] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 496 522 3507; e-mail: troshin2003@inbox.ru*
[b] *Ivanovo State University, 153025 Ivanovo, Russian Federation*

DOI: 10.1016/j.mencom.2015.07.016

A carbazole-to-fluorene ratio in the molecular structure of the title polymers was found to have a strong effect on the morphology of their composites with the fullerene derivatives ([60]PCBM and [70]PCBM) and their photovoltaic performance.

Organic solar cells based on conjugated polymers demonstrate high power conversion efficiencies approaching 8–9% for the best material combinations.[1–5] Unfortunately, the most efficient electron donor materials undergo rapid photochemical degradation, which dramatically affects the operational stability of devices.[6,7–10] At the same time, long operation lifetimes were predicted for some less efficient conjugated polymers possessing very robust chemical structures. In particular, a lifetime exceeding seven years was estimated for the solar cells based on the carbazole–thiophene–benzothiadiazole copolymer PCDTBT.[11] It is also known that fluorene–thiophene–benzothiadiazole copolymers (*e.g.*, F8TBT or F10TBT) demonstrate good operational stability and reasonably high photovoltaic performances.[12,13] In particular, fluorene-based polymers give excellent open circuit voltages of 900–1000 mV, which are substantially higher than those of carbazole-based polymers such as PCDTBT (~850 mV). According to theoretical models, fluorene-based copolymers should give ultimate efficiencies of 8.0–8.5% in organic solar cells.[14,15] Surprisingly, the best experimental result reported for the most promising material F10TBT (4.2%) was about two times lower than theoretical expectations.[16,17] At the same time, PCDTBT showed experimental efficiencies of 6.0–6.5%, which are very close to the theoretical maximum for this system.[3,18–20]

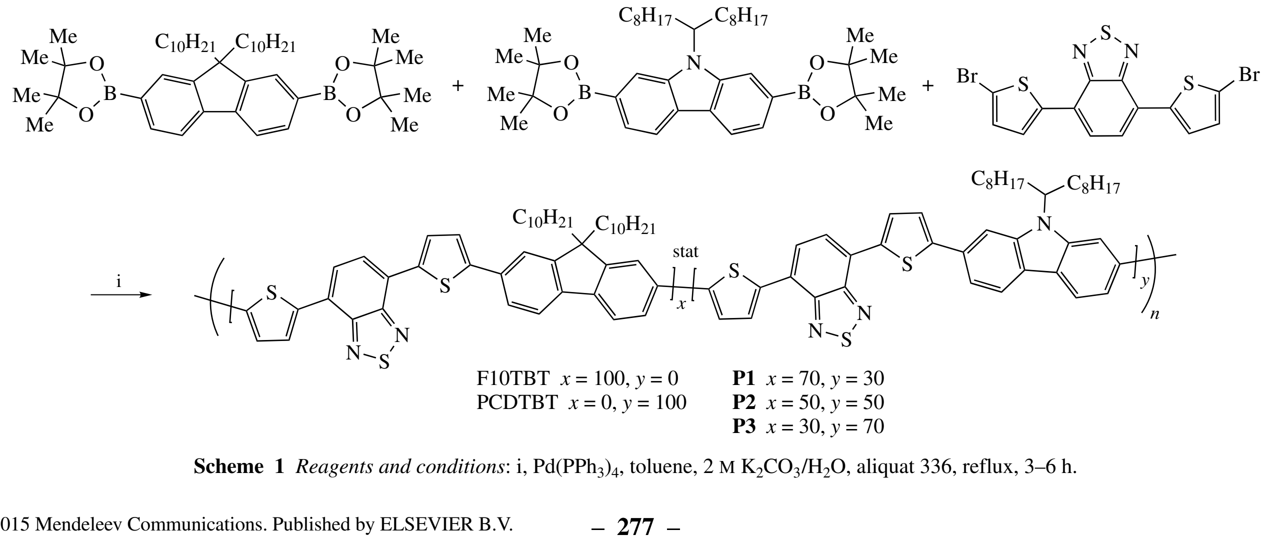
In order to understand the fundamental differences in the behaviors of F10TBT and PCDTBT in organic solar cells, we synthesized and characterized these two polymers and three hybrid statistical copolymers **P1**–**P3** (Scheme 1). Note that statistical copolymers are intensively investigated as promising electron-donor materials for organic solar cells.[21] As reported previously, fluorene–carbazole–thiophene–benzothiadiazole copolymers can have solar cell efficiencies approaching 4–5%.[22,23]

The Suzuki polycondensation was used to obtain the samples of F10TBT, PCDTBT and **P1**–**P3** with high molecular weights and reasonable polydispersities (Table 1). The synthesized polymers showed slightly different optical properties in solution (Figure S1, Online Supplementary Materials). In particular, the absorption maximum of **P3** is shifted by about 10 nm towards longer wavelengths in comparison with F10TBT. This reflects the electronic effects coming from the introduction of carbazole units to the polymer chains. Similar differences were observed in the spectra of thin films [Figure 1(*a*)]. PCDTBT revealed the broadest absorption band with the edge shifted towards long wavelengths compared to the other polymers. On the contrary, F10TBT

Table 1 Optoelectronic properties of conjugated polymers.

Polymer	M_w/ g mol^{-1}	M_w/M_n	λ_{max} solution/ nm	λ_{max} film/nm	HOMO[a]/ eV	LUMO[b]/ eV	E_g^c/eV
F10TBT	135000	2.7	560	565	–5.68	–3.80	1.88
P1	135000	4.6	560	569	–5.68	–3.82	1.86
P2	180000	3.1	565	575	–5.64	–3.80	1.84
P3	103000	2.9	570	576	–5.60	–3.76	1.84
PCDTBT	210000	3.0	575	576	–5.50	–3.70	1.80

[a] HOMO energies were estimated from the onsets of oxidation waves in the cyclic voltammograms of thin polymer films [see Figure 1(*b*)]. [b] LUMO energy was calculated as E(HOMO) + E_g. [c] E_g was determined from the onset of the absorption edge at long wavelengths.



Scheme 1 *Reagents and conditions*: i, Pd(PPh$_3$)$_4$, toluene, 2 M K$_2$CO$_3$/H$_2$O, aliquat 336, reflux, 3–6 h.

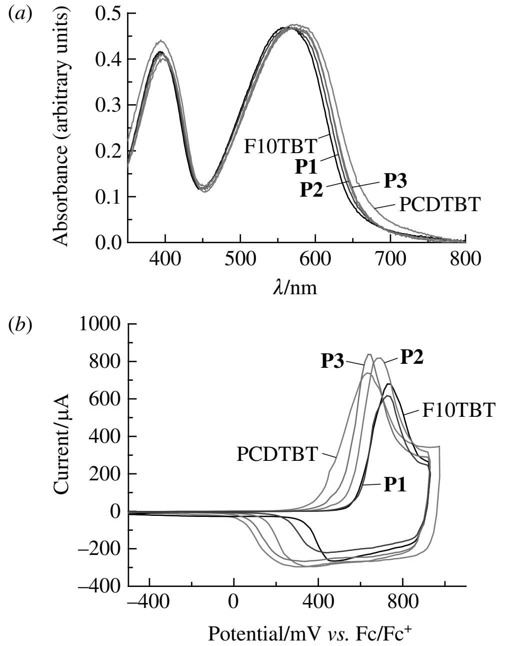


Figure 1 (*a*) Thin-film absorption spectra of F10TBT, PCDTBT and **P1**–**P3** and (*b*) their cyclic voltammograms.

demonstrated the narrowest absorption band corresponding to the widest optical band gap of this material. The spectra of statistical copolymers **P1**–**P3** compromised the optical properties of the parent polymers F10TBT and PCDTBT. The observed differences in the optical properties can be due to the intermolecular interactions of neighboring polymer chains in the films (π–π stacking).

The electrochemical properties were investigated for solid polymer films deposited directly on glassy carbon disc electrodes (see Online Supplementary Materials). The cyclic voltammograms are shown in Figure 1(*b*). The polymers F10TBT and **P1** demonstrated the highest oxidation potentials. An increase in the carbazole content of the polymers leads to the lowering of their oxidation potentials in the order F10TBT ~ **P1** > **P2** > **P3** > > PCDTBT. The onset potentials of the polymer oxidation waves ($E^{\mathrm{ox}}_{\mathrm{onset}}$) were used for estimating the HOMO energy levels of the materials according to the well-established procedure (Fermi energy of –5.1 eV was used for the Fc$^+$/Fc couple).[24] The data given in Table 1 illustrate a decrease in the HOMO energies of the polymers with the concentration of fluorene units in the molecular structures of the materials. According to the electrochemical data, the polymers F10TBT and **P1** are expected to exhibit the highest open circuit voltages in organic solar cells due to their deep lying HOMO energy levels.[25]

The photovoltaic properties of the polymers were studied in a conventional bulk heterojunction solar cell architecture using the fullerene derivatives [60]PCBM and [70]PCBM as electron-acceptor counterparts (Figure 2).[†]

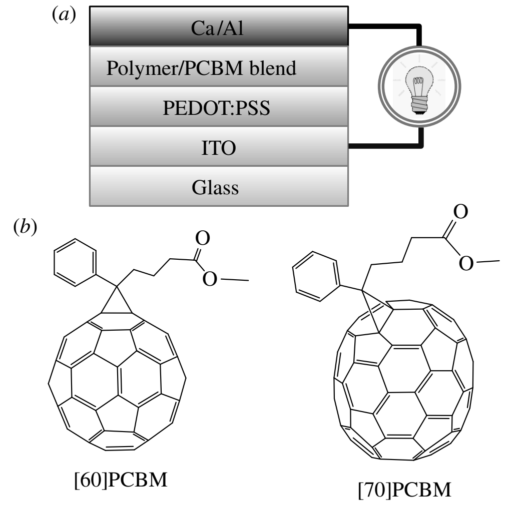


Figure 2 (*a*) Schematic layout of an organic solar cell and (*b*) molecular structures of [60]PCBM and [70]PCBM used as electron-acceptor components.

The current–voltage (J–V) characteristics and external quantum efficiency (EQE) spectra of the devices based on different materials are shown in Figure 3. Data in Table S1 (Online Supplementary Materials) and Figures 3 and 4 indicate that the open circuit voltage of organic solar cells decreases with the concentration of carbazole units in the electron donor polymers. However, the short circuit current density J_{SC} goes an opposite trend and reaches a maximum for PCDTBT. As a result, polymers **P2** and **P3** give considerably higher power conversion efficiencies in solar cells, as compared

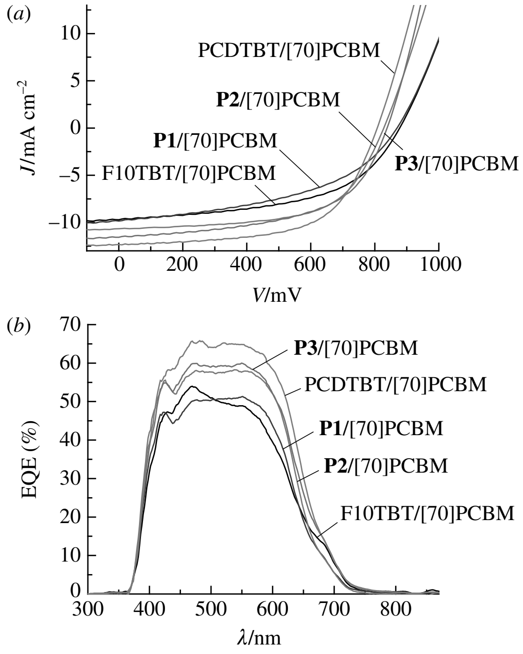


Figure 3 (*a*) J–V characteristics of solar cells comprising polymers F10TBT, PCDTBT and **P1**–**P3** and (*b*) their EQE spectra.

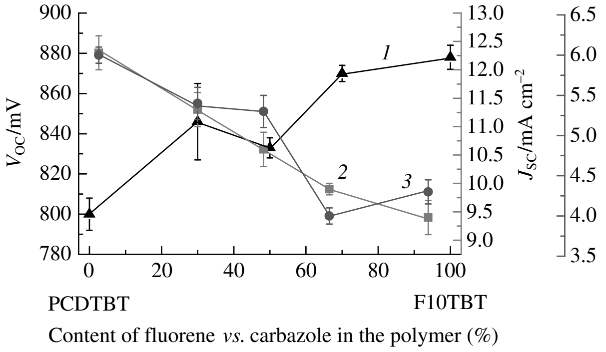


Figure 4 (*1*) Open cirquit voltage, V_{OC}, (*2*) short cirquit current density, J_{SC}, and (*3*) power conversion efficiency, *η*, of organic solar cells based on the polymer/[70]PCBM blends as functions of the polymer composition.

[†] A conjugated polymer and a fullerene derivative were dissolved in 1,2-dichlorobenzene with continuous stirring at 45 °C for 48 h. Afterwards, an appropriate amount of 1,6-diiodohexane (processing additive) was added (see Table S1) and the blend solution was filtered through a PTFE syringe filter (0.45 μm). The active layer was deposited on ITO slides covered with PEDOT : PSS (60 nm) by the spin-coating of fullerene–polymer blends with the subsequent annealing at 95 °C for 10 min. The devices were finalized by the evaporation of top Ca (20 nm) and Al (100 nm) electron-collecting electrode *in vacuo* (1×10^{-6} mbar).

to those of F10TBT and **P1**, while the best efficiencies are obtained for PCDTBT (Figure 4). Note that the use of 1,6-diiodohexane (DIH) as a processing additive considerably improved the photovoltaic performance of the **P2**/[70]PCBM blends, while other binary systems were tolerant to the presence of DIH.

Figure 4 clearly illustrates a high potential of statistical copolymerization as a technique for the fine tuning of electronic and photovoltaic parameters of photoactive materials for organic solar cells. This approach is especially valuable for tailoring the optoelectronic properties of conjugated polymers used in the front and back subcells of tandem double-junction devices.[15]

The efficiencies of the solar cells based on the polymers F10TBT, PCDTBT and **P1**–**P3** can be strongly affected by the morphology of their blends with the fullerene derivatives [60]PCBM and [70]PCBM used as electron acceptor components.[26] We studied the surface topography of the polymer/[70]PCBM blends using atomic force microscopy (AFM) (Figure S2, Online Supplementary Materials). The F10TBT/[70]PCBM films exhibited a featureless structure suggesting that both components are strongly intermixed in the blend. The intimate intermixing of the fullerene and polymer in the active layer of the device facilitates the photoinduced charge generation but strongly inhibits the transport of free charges towards respective electrodes. This might be a reason why the solar cells based on F10TBT and other polymers with high fluorene loadings demonstrate decreased short circuit current densities. An increase in the concentration of carbazole units in the polymer chains results in the appearance of nanometer-sized clusters in the films suggesting that polymer and fullerene derivative undergo optimal phase separation facilitating both charge generation and transport to the electrodes. The most ordered films were revealed for the PCDTBT/[70]PCBM blends thus explaining their advanced photovoltaic performance.

The microscopy data imply that non-balanced active layer morphology is a major reason for the insufficiently high photovoltaic performance of F10TBT and related fluorene-based copolymers. This problem can be solved using alternative fullerene-based acceptor materials possessing different solubility and/or molecular compatibility with the polymers.[27]

Thus, we synthesized and systematically investigated five conjugated copolymers comprising TBT units (T is thiophene, and B is benzothiadiazole) linked with carbazole and/or fluorene fragments. A variation in the fluorene-to-carbazole ratio in the polymer chains affects optical and electrochemical properties of these materials. Moreover, the composition of the polymers strongly influences the morphology of their blends with the fullerene derivative ([70]PCBM) and their performance in organic solar cells. The statistical copolymerization in general was found a powerful approach to tailoring the optoelectronic properties of photoactive materials designed for photovoltaic applications.

This work was supported by the Russian Science Foundation (grant no. 14-13-01031). We are grateful to A. V. Akkuratov for his assistance in performing some experiments.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.07.016.

References

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.

2 M. Zhang, Y. Gu, X. Guo, F. Liu, S. Zhang, L. Huo, T. Russell and J. Hou, *Adv. Mater.*, 2013, **25**, 4944.

3 Z. He, C. Zhong, X. Huang, W. Wong, H. Wu, L. Chen, S. Su and Y. Cao, *Adv. Mater.*, 2011, **23**, 4636.

4 Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 591.

5 C. Cabanetos, A. Labban, J. Bartelt, J. Douglas, W. Mateker, J. Frechet, M. McGehee and P. Beaujuge, *J. Am. Chem. Soc.*, 2013, **135**, 4656.

6 M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen and F. C. Krebs, *Adv. Mater.*, 2012, **24**, 580.

7 V. A. Kostyanovsky, D. K. Susarova, G. Adam, R. N. Lyubovskaya and P. A. Troshin, *Mendeleev Commun.*, 2013, **23**, 26.

8 Y. W. Soon, H. Cho, J. Low, H. Bronstein, I. McCulloch and J. R. Durrant, *Chem. Commun.*, 2013, **49**, 1291.

9 E. A. A. Arbab, B. Taleatu and G. T. Mola, *J. Mod. Opt.*, 2014, **61**, 1749.

10 L. A. Frolova, N. P. Piven, D. K. Susarova, A. V. Akkuratov, S. D. Babenko and P. A. Troshin, *Chem. Commun.*, 2015, **51**, 2242.

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

12 F. Zhang, K. G. Jespersen, C. Björström, M. Svensson, M. R. Andersson, V. Sundström, K. Magnusson, E. Moons, A. Yartsev and O. Inganäs, *Adv. Funct. Mater.*, 2006, **16**, 667.

13 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.

14 M. C. Scharber, D. Muhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, **18**, 789.

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

16 D. Di Nuzzo, G.-J. A. H. Wetzelaer, R. K. M. Bouwer, V. S. Gevaerts, S. C. J. Meskers, J. C. Hummelen, P. W. M. Blom, and R. A. J. Janssen, *Adv. Energy Mater.*, 2013, **3**, 85.

17 D. Veldman, O. Ipek, S. C. J. Meskers, J. Sweelssen, M. M. Koetse, S. C. Veenstra, J. M. Kroon, S. S. van Bavel, J. Loos and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2008, **130**, 7721.

18 S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297.

19 J. H. Seo, A. Gutacker, Y. Sun, H. Wu, F. Huang, Y. Cao, U. Scherf, A. J. Heeger and G. C. Bazan, *J. Am. Chem. Soc.*, 2011, **133**, 8416.

20 G. Fang, J. Liu, Y. Fu, B. Meng, B. Zhang, Z. Xie and L. Wang, *Org. Electron.*, 2012, **13**, 2733.

21 (*a*) B. Xu, S. Noh and B. C. Thompson, *Macromolecules*, 2014, **47**, 5029; (*b*) 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 and S. Cho, *Energy Environ. Sci.*, 2012, **5**, 9803; (*c*) L. Fang, Y. Zhou, Y.-X. Yao, Y. Diao, W.-Y. Lee, A. L. Appleton, R. Allen, J. Reinspach, S. C. B. Mannsfeld and Z. Bao, *Chem. Mater.*, 2013, **25**, 4874; (*d*) J. W. Jung, F. Liu, T. P. Russell and W. H. Jo, *Energy Environ. Sci.*, 2013, **6**, 3301; (*e*) T. E. Kang, H.-H. Cho, H. j. Kim, W. Lee, H. Kang and B. J. Kim, *Macromolecules*, 2013, **46**, 6806; (*f*) P. P. Khlyabich, B. Burkhart, C. F. Ng and B. C. Thompson, *Macromolecules*, 2011, **44**, 5079; (*g*) J.-M. Jiang, H.-C. Chen, H.-K. Lin, C.-M. Yu, S.-C. Lan, C.-M. Liu and K.-H. Wei, *Polym. Chem.*, 2013, **4**, 5321; (*h*) D. Kotowski, S. Luzzati, G. Bianchi, A. Calabrese, A. Pellegrino, R. Po, G. Schimperna and A. Tacca, *J. Mater. Chem. A*, 2013, **1**, 10736; (*i*) J. Li, K.-H. Ong, S.-L. Lim, G.-M. Ng, H.-S. Tan and Z.-K. Chen, *Chem. Commun.*, 2011, **47**, 9480; (*j*) 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 and C.-S. Hsu, *Adv. Mater.*, 2014, **26**, 5205.

22 S. J. Park, J. M. Cho, W.-B. Byun, J.-C. Lee, W. S. Shin, I.-N. Kang, S.-J. Moon and S. K. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 4416.

23 Y. Fu, H. Cha, G.-Y. Lee, B. J. Moon, C. E. Park and T. Park, *Macromolecules*, 2012, **45**, 3004.

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

25 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.

26 P. A. Troshin and N. S. Sariciftci, in *Organic Nanomaterials: Synthesis, Characterization, and Device Applications*, eds T. Torres and G. Bottari, John Wiley & Sons, Inc., Hoboken, NJ, 2013, ch. 25, pp. 549–578.

27 (*a*) P. A. Troshin, O. A. Mukhacheva, O. Usluer, S. Rathgeber, A. E. Goryachev, A. V. Akkuratov, D. K. Susarova, N. S. Sariciftci, V. F. Razumov and D. A. M. Egbe, *Adv. Energ. Mater.*, 2013, **3**, 161; (*b*) P. A. Troshin, O. A. Mukhacheva, A. E. Goryachev, N. N. Dremova, D. Voylov, C. Ulbricht, D. A. M. Egbe, N. S. Sariciftci and V. F. Razumov, *Chem. Commun.*, 2012, **48**, 9477; (*c*) P. A. Troshin, D. K. Susarova, E. A. Khakina, A. E. Goryachev, O.V. Borshchev, S. A. Ponomarenko, V. F. Razumov and N. S. Sariciftci, *J. Mater. Chem.*, 2012, **22**, 18433; (*d*) J. Y. Mayorova, S. L. Nikitenko, P. A. Troshin, S. M. Peregudova, A. S. Peregudov, M. G. Kaplunov and R. N. Lyubovskaya, *Mendeleev Commun.*, 2007, **17**, 175; (*e*) P. A. Troshin, I. P. Romanova, D. K. Susarova, G. G. Yusupova, A. T. Gubaidullin, A. F. Saifina, V. V. Zverev, R. N. Lyubovskaya, V. F. Razumov and O. G. Sinyashin, *Mendeleev Commun.*, 2010, **20**, 137.

Received: 15th December 2014; Com. 14/4527