

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

# ESR spectroscopy as a powerful tool for probing the quality of conjugated polymers designed for photovoltaic applications

Diana K. Susarova,<sup>a</sup> Nataliya P. Piven,<sup>b</sup> Alexander V. Akkuratov,<sup>a</sup> Lyubov A. Frolova,<sup>a</sup> Marina S. Polinskaya,<sup>c</sup> Sergey A. Ponomarenko,<sup>c</sup> Sergey D. Babenko,<sup>b</sup> and Pavel A. Troshin\*<sup>a</sup>

5 Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Here we report the application of the Electron Spin Resonance (ESR) spectroscopy as a highly sensitive analytical technique for assessment of the electronic quality of organic semiconductor materials, particularly conjugated polymers. It has been shown that different batches of the same conjugated polymer might contain substantially different amounts of radical species which were attributed to structural defects and/or impurities behaving as traps for mobile charge carriers. Good correlations between the concentrations of radicals in various batches of conjugated polymers and their performances in organic solar cells have been revealed.

Conjugated polymers represent nowadays a family of high-performance materials for organic solar cells, light emitting diodes, field-effect transistors, photodetectors, sensors and other types of electronic devices.<sup>1</sup> Poor reproducibility of physical and electronic properties of polymer-based semiconductors is one of the most significant drawbacks for their industrial implementation. Different samples of the same polymer might differ by the molecular weight characteristics, concentrations of defects and chemical impurities, charge carrier mobilities and etc. As a result, different batches of conjugated polymers might perform quite differently in organic electronic devices, in particular, solar cells.<sup>2</sup>

Conjugated polymers are usually designed using palladium catalyzed cross-coupling reactions, e.g. Suzuki or Stille polycondensation routes.<sup>3</sup> The impurities resulting from the catalyst decomposition, e.g. palladium nanoparticles, affect strongly electrical performance of the resulting material.<sup>4</sup> Purification of conjugated polymers requires application of specific reagents and might be still challenging.<sup>5</sup>

Besides the residual palladium, polymers might be polluted with small amounts of starting reagents (e.g. boronic acids) or have some chemically active functions such as -B(OH)<sub>2</sub> or halogen atoms as end groups on the polymer backbone. At the same time, conjugated polymers typically undergo rapid oxidation in air breaking their conjugated backbones and producing active oxygen-containing species (hydroxyl, ketone or carboxyl functions). Alternatively, polymers can be doped easily with electron deficient molecules (e.g. halogens, oxygen).<sup>6</sup> All these processes result in degradation of

semiconductor properties of conjugated polymers.

The problem becomes even more severe due to insufficient sensitivity of the most common analytical methods (e.g. NMR, HPLC, FTIR, chemical analysis and etc.) which can hardly be applied for characterization of conjugated polymers. Therefore, there is a strong demand for novel techniques which could reveal trace impurities and structural defects affecting electrical properties of conjugated polymers. We reported previously the application of impedance measurements for this purpose.<sup>7</sup> However, this approach is rather complicated and time consuming and can hardly be applied to many polymer samples.

Here we report the application of the ESR spectroscopy as a simple tool for assessment of the electronic quality of different batches of conjugated polymers. The ESR spectroscopy was applied previously for investigation of the photoinduced charge separation in the fullerene/polymer blends,<sup>8</sup> charge recombination kinetics,<sup>9</sup> degradation of conjugated polymers in air,<sup>10</sup> and revealing the traps for mobile charge carries in inorganic nanocrystals.<sup>11</sup> In the present work we used ESR spectroscopy to characterize more than fifty batches of eleven different conjugated polymers whose molecular structures are shown in Fig. 1.

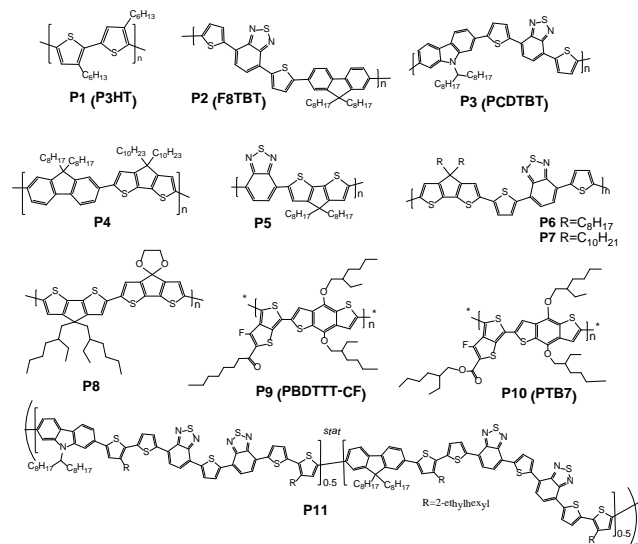


Figure 1. Molecular structures of investigated polymers

The information regarding the preparation and characteristics of the investigated polymer samples is provided in Electronic supplementary information (ESI). Conjugated polymers P1-P12 (Fig. 1) do not incorporate any spin-active units in their molecular frameworks. Therefore, no signals should be expected in their ESR spectra. On the contrary, the experimental ESR spectra of almost all polymer samples measured in dark at room temperature revealed the presence of the radical species. The concentrations of such species could differ significantly for different batches of the same polymer. This effect is clearly illustrated in Fig. 2 by exemplary sets of the ESR spectra obtained for various samples of polymers P1 (P3HT) and P2 (F8TBT). It should be noted that these spectra are normalized to the weight of the material; therefore, the intensity of the observed signals reflects the concentrations of the radical species in the analyzed polymer samples.

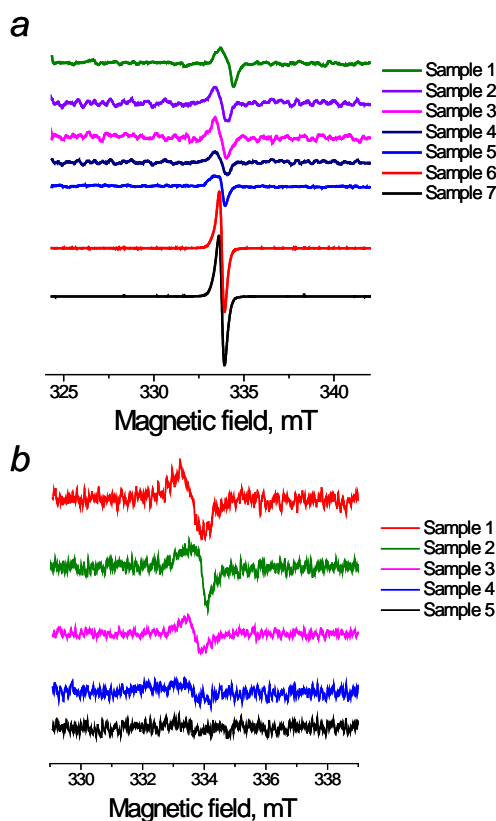


Figure 2. The ESR spectra of different batches of P1 (P3HT) (a) and P2 (F8TBT) (b) normalized to the weight of the material.

We strongly believe that appearance of the signals in the dark ESR spectra of conjugated polymers is related to the presence of some structural defects or chemical impurities possessing unpaired electrons. These radical species are expected to behave as deep traps for mobile charge carriers thus affecting electrical performance of conjugated polymers in devices. In order to prove this hypothesis, we have investigated the performance of all samples of conjugated polymers in bulk heterojunction solar cells using [60]PCBM or [70]PCBM as electron acceptor counterparts (both acceptors did not show ESR signals). It has been shown that different batches of

the same polymer reveal different photovoltaic performances which correlate well with the respective concentrations of the radical species. It is seen from the Fig. 3 that efficiency of the solar cells based on PCDTBT/[60]PCBM composites decreases with increase in the concentration of the radical species  $C_R$  in the polymer defined as a number of spins per gram (spin/g).

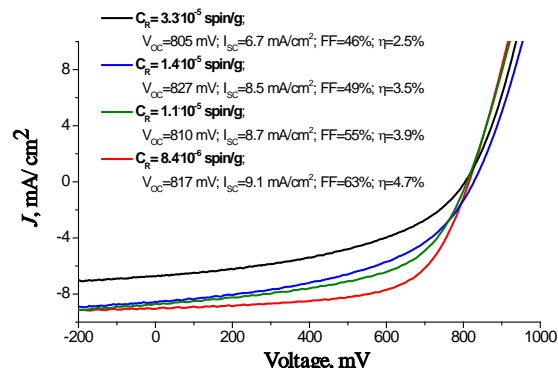


Figure 3. J-V curves for organic bulk heterojunction solar cells based on different batches of PCDTBT (with different  $C_R$ ) blended with [60]PCBM

Very similar results were also obtained for other investigated conjugated polymers. Fig. 4 shows that P1 (P3HT), P2 (F8TBT) and P3 (PCDTBT) behave rather similarly. The experimental points can be approximated reasonably well by linear dependences. It is very likely that sensitivity of the polymers towards the presence of radical species is influenced to some extent by peculiarities of their molecular structures and their optoelectronic properties. Therefore, the same concentration of radicals deteriorates the photovoltaic performance of different conjugated polymers to a different extent. This effect might explain different slope of the linear fit obtained for PCDTBT as compared to P3HT and F8TBT.

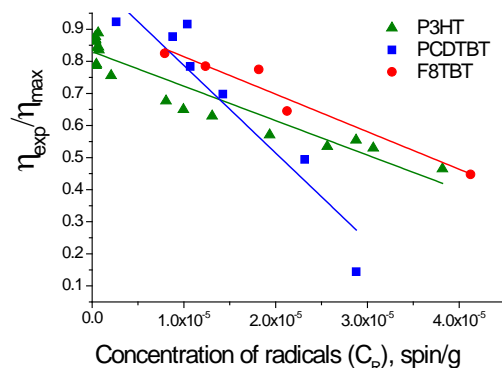


Figure 4. The influence of the radical species on the photovoltaic performance of conjugated polymers P1-P3.

It is known that various conjugated polymers might show distinctly different optoelectronic properties and, therefore, yield very different performances in organic solar cells (even if their properties are not affected by impurities or defects). For instance, the solar cells based on P3HT/[60]PCBM blends give reproducible power conversion efficiencies of ca. 4.0%. At the same time, PCDTBT/[60]PCBM and PCDTBT/[70]PCBM systems yield  $\eta$  of  $\sim 5.0\%$  and  $\sim 6.5\%$ ,

respectively. The PTB7/[70]PCBM blends reveal efficiencies of 7-8%. For purpose of comparison of different systems we introduce here “normalized efficiency” of solar cells defined as  $\eta_{\text{exp}}/\eta_{\text{max}}$ , where  $\eta_{\text{exp}}$  is experimentally obtained efficiency of organic solar cells based on a certain batch of the material, while  $\eta_{\text{max}}$  is the estimated ultimate performance of this material. The latter value is taken from the literature as the highest reproducible efficiency of a certain material obtained in the same device architecture or calculated using theoretical approach presented by Scharber et. al.<sup>12</sup> if experimental data are not available. The  $\eta_{\text{exp}}$  and  $\eta_{\text{max}}$  values for all polymer samples used in this study are given in Table S1 (See Electronic Supplementary Information, ESI) together with the determined concentrations of the radical species  $C_R$ .

Fig. 5 illustrates the influence of radical impurities and defects on photovoltaic performance of different conjugated polymers. It should be emphasized that this graph summarizes the data obtained for 58 batches of 11 structurally different conjugated polymers. It is seen from this graph that few polymer samples characterized by  $\log(C_R)$  lying in the range between -1.5 and -3.5 demonstrate very low photovoltaic performance presumably due to massive trapping of charge carriers. The photovoltaic performance of the samples characterized by  $\log(C_R)$  lying between -4.75 and -3.5 depends strongly on the structure and properties of conjugated polymers. Some polymers which are less sensitive with respect to the radical species (e.g. P3HT) might demonstrate reasonably good photovoltaic performance. On the contrary, the photovoltaic performance of more sensitive materials (e.g. PCDTBT) deteriorates dramatically when  $\log(C_R)$  approaches the level of ca. -4.5. Finally, all batches of conjugated polymers characterized by  $\log(C_R) < -5$  demonstrate appreciably good photovoltaic performance. Therefore, the concentrations of the radical species in the samples of conjugated polymers have to be kept below  $\sim 10^{-5}$  spins per gram in order to achieve the best solar cell efficiencies.

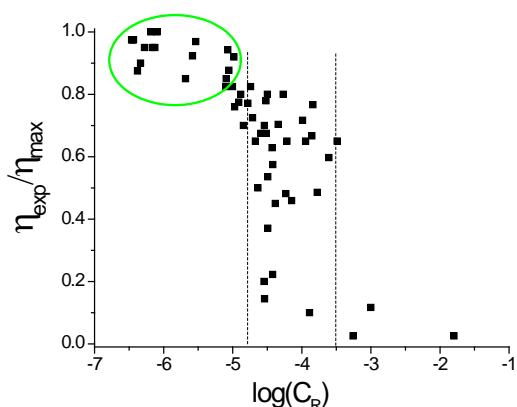


Figure 5. Influence of the radical impurities and defects on photovoltaic performance of conjugated polymers

It is known that the efficiency of organic solar cells might be affected by multiple parameters such as fullerene-polymer ratio, active layer morphology, active layer thickness, quality of contacts and interfaces, presence of ESR-silent impurities, molecular weights and polydispersity of polymers and etc.

However, if the listed above parameters are optimized, the concentration of the radical species can be considered as a crucially important factor governing the photovoltaic performance of conjugated polymers.

In conclusion, we have shown that ESR spectroscopy can be used as a very informative and simple technique for assessment of quality of different conjugated polymers applied as electron donor materials for organic solar cells. This method might be considered as a potentially very useful tool for probing the quality of different types of semiconductor materials used in organic electronics.

This work was supported by the Russian Science Foundation (grant No. 14-13-01031). We gratefully acknowledge participation of Dr. V. A. Kostyanovskiy in the synthesis of some polymers and thank Prof. A. V. Kulikov for helpful discussions.

## Notes and references

- <sup>a</sup> IPCP RAS, Semenov Prospect 1, Chernogolovka, 141432, Russia. Fax: +7 496515-5420; Tel: +7 496522 1418; E-mail: [troshin2003@inbox.ru](mailto:troshin2003@inbox.ru)
- <sup>b</sup> Institute of Energy Problems for Chemical Physics (Branch) RAS, Semenov Prospect 1, Chernogolovka, 142432, Russia
- <sup>c</sup> ISPM RAS, 70 ul. Profsoyuznaya, Moscow 117393, Russia
- † Electronic Supplementary Information (ESI) available: Numerical data on the concentrations of radical species in the analyzed samples of conjugated polymers and their photovoltaic performances. See DOI: 10.1039/b000000x/
- 1 H. Klauk Ed., Organic Electronics II: More Materials and Applications. WILEY VCH, 2012; D. S. Correa, E. S. Medeiros, J. E. Oliveira, L. G. Paterno, L. H. C. Mattoso, *J. Nanosci. Nanotech.* 2014, **14**, 6509; L. Ye, S. Zhang, L. Huo, M. Zhang, J. Hou, *Acc. Chem. Res.* 2014, **47**, 1595; X. Guo, M. Baumgarten, K. Müllen. *Prog. Polym. Sci.* 2013, **38**, 1832; J. Chen, Y. Cao, *Acc. Chem. Res.* 2009, **42**, 1709.
- 2 H. K. H. Lee, Z. Li, I. Constantinou, F. So, S. W. Tsang S. K. So. *Adv. Energ. Mater.* 2014, **4**, 10.1002/aenm.201400768
- 3 Design and Synthesis of Conjugated Polymers, M. Leclerc and J. F. Morin Eds., WILEY VCH, 2010.
- 4 Krebs, F. C.; Nyberg, R. B.; Jørgensen, M. *Chem. Mater.* 2004, **16**, 1313.
- 5 K. T. Nielsen, K. Bechgaard, F. C. Krebs, *Macromolecules* 2005, **38**, 658; K.T. Nielsen, K. Bechgaard, F.C. Krebs, *Synthesis* 2006, **10**, 1639.
- 6 Handbook of Conducting Polymers, Third Edition, Conjugated Polymers: Theory, Synthesis, Properties, and Characterization. T. A. Skotheim and J. Reynolds Eds., CRS Press, 2006; M. Jørgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.* 2012, **24**, 580.
- 7 P. A. Troshin, D. K. Susarova, Y. L. Moskvina, I. E. Kuznetsov, S. A. Ponomarenko, E. N. Myshkovskaya, K. A. Zakharcheva, A. A. Balakai, S. D. Babenko, V. F. Razumov. *Adv. Funct. Mater.* 2010, **20**, 4351
- 8 L. Franco, A. Toffoletti, M. Ruzzi, L. Montanari, C. Carati, L. Bonoldi, R. Po. *J. Phys. Chem. C*, 2013, **117**, 1554; N. Camaioni, F. Tinti, L. Franco, M. Fabris, A. Toffoletti, M. Ruzzi, L. Montanari, L. Bonoldi, A. Pellegrino, A. Calabrese, R. Po. *Org. Electronics* 2012, **13**, 550.
- 9 H. Tanaka, N. Hasegawa, T. Sakamoto, K. Marumoto, S. I. Kuroda, *Jap. J. Appl. Phys. I*, 2007, **46**, 5187.
- 10 A. Sperlich, H. Kraus, C. Deibel, H. Blok, J. Schmidt, V. Dyakonov, *J. Phys. Chem. B*, 2011, **115**, 13513; A. Konkin, H.-K. Roth, P. Scharff, A. Aganov, O. Ambacher, S. Sensfuss. *Sol. State Commun.* 2009, **149**, 893.
- 11 D. J. Keeble, E. A. Thomsen, A. Stavrinadis, I. D.W. Samuel, J. M. Smith, A. A.R. Watt. *J. Phys. Chem. C* 2009, **113**, 17306.
- 12 M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec. *Adv. Mater.* 2006, **18**, 789.