Molecular Ordering in the Solid State

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Ordering of PCDTBT Revealed by Time-Resolved Electron Paramagnetic Resonance Spectroscopy of Its Triplet Excitons**

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Abstract: *Time-resolved electron paramagnetic resonance (TREPR) spectroscopy is shown to be a powerful tool to characterize triplet excitons of conjugated polymers. The resulting spectra are highly sensitive to the orientation of the molecule. In thin films cast on PET film, the molecules' orientation with respect to the surface plane can be determined, providing access to sample morphology on a microscopic scale. Surprisingly, the conjugated polymer investigated here, a promising material for organic photovoltaics, exhibits ordering even in bulk samples. Orientation effects may significantly influence the efficiency of solar cells, thus rendering proper control of sample morphology highly important.*

Triplet excitons play a crucial role in organic photovoltaics (OPV).[1] They are promising candidates to prolong diffusion lengths of excitons and therefore improve device efficiency, as recombination from the triplet state is spin-forbidden. Therefore, characterizing and revealing the origin of triplet excitons in conjugated materials is of high interest and an important step towards a broader understanding of the primary photophysical and photochemical processes in organic photovoltaic devices leading to charge separation.[2]

Time-resolved electron paramagnetic resonance (TREPR) spectroscopy is particularly suited for this task, as it can directly probe and identify triplet excitons[3] and unambiguously discern them from charge-transfer (CT) states[4] as well as free polarons.[5] The shape of TREPR spectra of triplet excitons strongly depends on the (selective) population of each of the three triplet sublevels, which is a function of the origin of the triplet exciton.[6] Processes by which triplet excitons can be formed are intersystem crossing (ISC) from the singlet exciton, back electron transfer (BET) from the CT state, triplet–triplet energy transfer from acceptor to donor, and singlet fission.[1a,7] To disentangle the different spectral contributions of the triplet exciton signals from different origins, it is of high importance to thoroughly characterize as many of these separate signals as possible. Therefore, investigating pristine components is the first step to reveal the details of the photophysics and the photochemistry of blends comprising the polymer under investigation as one component, and therefore the organic solar cell devices built based on them.

The conjugated polymer investigated here, poly[*N*-9′-heptadecanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT, cf. Figure 1), is one very promising candidate of a whole group of newly developed polymers based on polycarbazoles.[8] PCDTBT is particularly interesting due to both its reported high power conversion efficiency (>7%) in combination with [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as acceptor[9] as well as its high stability even under oxygen atmosphere and elevated temperatures.[10] Thus, PCDTBT is increasingly replacing poly(3-hexylthiophene) (P3HT) as a benchmark material and it is a candidate for large-scale processing and device manufacturing for real-world applications.[11]

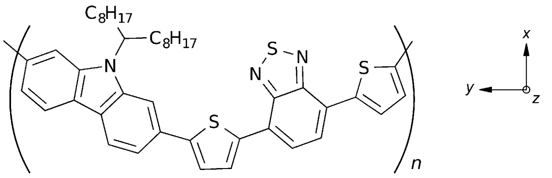

Figure 1. Molecular structure of PCDTBT. The axes represent the molecular coordinate system. Whereas the *z* axis points towards the reader, the *x*,*y* plane is parallel to the paper with arbitrary orientation of the *x* and *y* axes within this plane.

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In pristine PCDTBT, all channels forming the triplet exciton except ISC can be excluded as a source of the observed TREPR signal, as singlet fission would require a rather special arrangement of singlet and triplet energy levels to take place.[7a] The resulting TREPR spectrum of PCDTBT is shown in Figure 2, together with a spectral simulation based on the assumption of a single triplet-exciton species and no intrinsic orientation of the sample (full powder average). As can be clearly seen, the overall spectral shape is well accounted for by the simulation, except for the height of the outer "shoulders" of the spectrum.[12] Already this spectrum and its simulation give access to the crucial parameters D and E that parameterize the zero-field splitting tensor $\boldsymbol{D}$ originating from the triplet state[13] and clearly dominating the spectral width (see Figure 2). Furthermore, the spectral simulations reveal the zero-field populations of the three triplet sublevels fairly accurately (for details, see the Supporting Information).

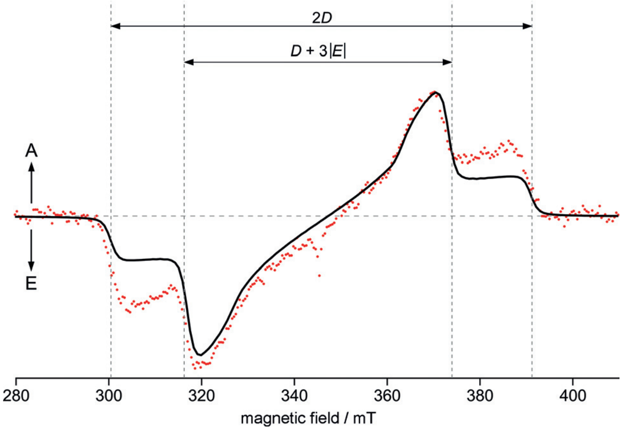

Figure 2. TREPR spectrum of PCDTBT (bulk sample) recorded 500 ns after pulsed-laser excitation together with a spectral simulation (black line). Due to its spectral width and shape, the signal can unambigously be identified as originating from a triplet exciton. As TREPR uses a direct detection scheme, the spectrum shows emissive (E) and enhanced absorptive (A) signals directly. For simulation parameters and experimental details see the Supporting Information.

One of the most obvious reasons for rationalizing the height of the shoulders of the PCDTBT triplet spectrum, which cannot be reproduced by simulations using a full powder average, is partial orientation. That is quite surprising, as PCDTBT is believed to be rather amorphous[14] only showing very short-range order,[15] in contrast to, for example, P3HT, which readily forms semicrystalline domains of variable size.[16] Interestingly, spectra of P3HT recorded under identical conditions can be fully accounted for by spectral simulations based on a single triplet species and a fully disordered sample, including the shoulders (see the Supporting Information for further details).

To further investigate this and to better control sample morphology, we drop-cast PCDTBT onto polyethylene terephthalate (PET, HOSTAPHAN RNK) film and recorded TREPR spectra at different angles of the film with respect to the direction of the external magnetic field. The results are shown in Figure 3, together with spectral simulations from a global fit of the parameters assuming a fixed relation between the different angular positions. To account for the partial orientation, a Gaussian distribution with standard deviation σ, centered about θ, one of the Euler angles (θ, ϕ) of the powder average, is used to weight the intensities accordingly. This allows for directly revealing both the preferred orientation and the degree of ordering in the sample for each position of the sample with respect to the external magnetic field. The spectral simulations fit the experimental data very well, particularly given that all spectra were fitted globally with only one set of parameters.

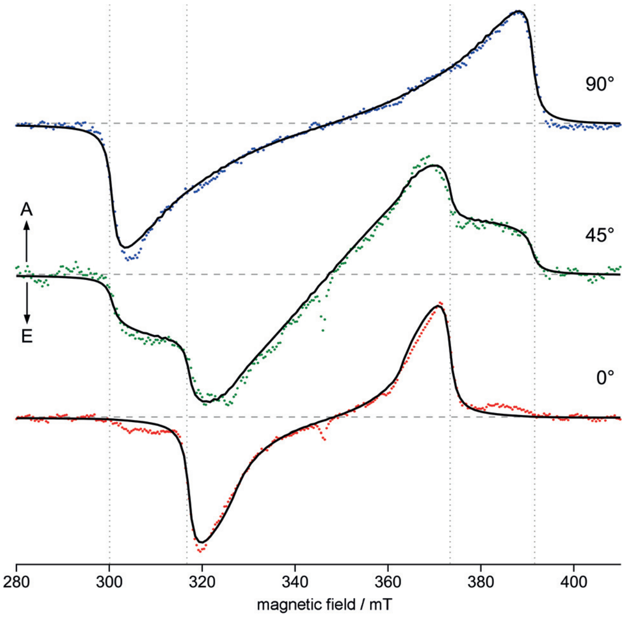

Figure 3. TREPR spectra of drop-cast PCDTBT, recorded 500 ns after pulsed-laser excitation at selected angles of the PET film with respect to the external magnetic field $\boldsymbol{B}_0$ together with spectral simulations (black lines) based on a global fit. For details see the Supporting Information.

To our surprise, the PCDTBT film shows clear orientational effects when drop-cast on PET film, as can be seen readily from the spectra (Figure 3). Furthermore, the full set of spectra recorded at angular positions between 0 and 180° (see the Supporting Information for further details) reveals unambiguously a C_{2v} symmetry, implying that the rotation axis of the sample is perpendicular to one of the axes of the dipolar coupling tensor $\boldsymbol{D}$ (of the triplet state). In our case, the rotation axis lies within the plane of the PET film. Furthermore, the spectra clearly show extrema for orientations of the PET film plane parallel and perpendicular to the external magnetic field axis. This restricts the possible orientations of the $\boldsymbol{D}$ tensor in the sample to be either parallel or perpendicular to the film plane. Given that the $\boldsymbol{g}$ and $\boldsymbol{D}$ tensors are coaxial and the g_z axis is perpendicular to the aromatic plane of the molecule,[17] the simulations reveal a parallel orientation of the molecular x,y plane ("face-on" orientation) with respect to the film surface. Whereas the backbone shows no preferred orientation in the x,y plane, the

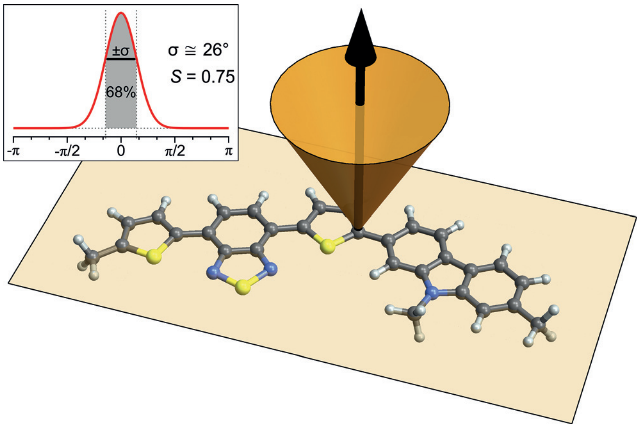

Figure 4. Graphical representation of the alignment of pristine PCDTBT drop-cast on PET film ("face-on" orientation). As can be clearly seen, the alignment is quite strong, with 68 % (±1 σ) of all molecules confined in the *z* direction within ±26 degrees (represented by the cone), equivalent to an ordering parameter $S=0.75$. Inset: Gaussian used to weight the powder average in the simulations.

alignment towards the *z* axis is quite strong, with about 68 % (±1 σ) of all molecules being oriented within ±26 degrees from the PET film plane normal (Figure 4). This corresponds to an order parameter $S=0.75$ meaning quite substantial axial orientation (see the Supporting Information for further details).

Both the ordering of thin films of PCDTBT and the molecular orientation ("face-on") on the surface are of high interest for applications in OPV devices, as their active layers are of comparable thickness to the films investigated here.

To the best of our knowledge, this is the first time TREPR has been used to probe the ordering of conjugated polymers. Only one study used optically detected magnetic resonance (ODMR) at very low temperatures (2.5 K) to determine the orientation of small molecules in a polystyrene matrix.[18] Given the high sensitivity of the shape of the triplet spectra to even slight preferential orientation of the molecules and the rather simple application of the method, TREPR opens up a plethora of new possibilities to probe the local morphology not only of pristine polymers but especially of polymer blends prepared in the same way as those used in photovoltaic devices.

In this work it could be shown that PCDTBT forms triplet states upon illumination with a short light pulse that manifest themselves in characteristic spectral signatures in TREPR spectroscopy. Drop-casting PCDTBT onto a PET surface leads to a rather strong macroscopic ordering in the sample that could be analyzed by recording TREPR spectra at different sample orientations with respect to the direction of the external magnetic field. Using spectral simulations, we could unequivocally demonstrate that PCDTBT has its aromatic ring plane oriented parallel to the PET surface ("face-on" orientation). Interestingly, even for bulk samples, only simulations taking a partial ordering of the sample into account can thoroughly reproduce the spectral shape of the signal. Given the known major role of morphology for device efficiency,[19] this clearly shows that controlling the sample morphology is of particular importance for EPR spectroscopic investigations of polymers used in organic photovoltaics. At the same time, these findings render TREPR spectroscopy a perfect tool to resolve the (local) morphology of these polymers even in blends with fullerenes or other polymers. Furthermore, given the different sources of triplet excitons with characteristic and distinguishable spectral shape, it is of high importance to first characterize the single components before proceeding to blends in order to reliably discern the spectral contributions from different triplet channels and gain insight into the primary photophysics and photochemistry of the blends under investigation.

Keywords: ordering · organic solar cells · PCDTBT · TREPR · triplet exciton

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[1] a) A. Rao, P. C. Y. Chow, S. Gélinas, C. W. Schlenker, C.-Z. Li, H.-L. Yip, A. K.-Y. Jen, D. S. Ginger, R. H. Friend, *Nature* **2013**, *500*, 435–439; b) A. Köhler, H. Bässler, *Mater. Sci. Eng. R* **2009**, *66*, 71–109.

[2] a) F. Gao, O. Inganäs, *Phys. Chem. Chem. Phys.* **2014**, *16*, 20291–20304; b) S. Few, J. M. Frost, J. Nelson, *Phys. Chem. Chem. Phys.* **2015**, *17*, 2311–2325.

[3] R. M. Kowalczyk, E. Schleicher, R. Bittl, S. Weber, *J. Am. Chem. Soc.* **2004**, *126*, 11393–11399.

[4] a) J. Behrends, A. Sperlich, A. Schnegg, T. Biskup, C. Teutloff, K. Lips, V. Dyakonov, R. Bittl, *Phys. Rev. B* **2012**, *85*, 125206; b) Y. Kobori, R. Noji, S. Tsuganezawa, *J. Phys. Chem. C* **2013**, *117*, 1589–1599; c) Y. Kobori, T. Miura, *J. Phys. Chem. Lett.* **2015**, *6*, 113–123.

[5] a) V. I. Krinichnyi, E. I. Yudanova, N. G. Spitsina, *J. Phys. Chem. C* **2010**, *114*, 16756–16766; b) K. Marumoto, Y. Muramatsu, N. Takeuchi, S. Kuroda, *Synth. Met.* **2003**, *135*, 433–434; c) O. G. Poluektov, S. Filippone, N. Martín, A. Sperlich, C. Deibel, V. Dyakonov, *J. Phys. Chem. B* **2010**, *114*, 14426–14429; d) S. Sensfuss, A. Konkin, H.-K. Roth, M. Al-Ibrahim, U. Zhokhavets, G. Gobsch, V. I. Krinichnyi, G. A. Nazmutdinova, E. Klemm, *Synth. Met.* **2003**, *137*, 1433–1434; e) G. Zoriniants, V. Dyakonov, M. Scharber, C. J. Brabec, R. A. J. Janssen, J. C. Hummelen, N. S. Sariciftci, *Synth. Met.* **1999**, *102*, 1241–1242.

[6] D. E. Budil, M. C. Thurnauer, *Biochim. Biophys. Acta* **1991**, *1057*, 1–41.

[7] a) M. B. Smith, J. Michl, *Chem. Rev.* **2010**, *110*, 6891–6936; b) B. Z. Tedlla, F. Zhu, M. Cox, J. Drijkoningen, J. Manca, B. Koopmans, E. Goovaerts, *Adv. Energy Mater.* **2015**, *5*, 1401109.

[8] a) N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletête, G. Durocher, Y. Tao, M. Leclerc, *J. Am. Chem. Soc.* **2008**, *130*, 732–742; b) S. H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nat. Photonics* **2009**, *3*, 297–303.

[9] Y. Sun, C. J. Takacs, S. R. Cowan, J. H. Seo, X. Gong, A. Roy, A. J. Heeger, *Adv. Mater.* **2011**, *23*, 2226–2230.

[10] S. Cho, J. H. Seo, S. H. Park, S. Beaupré, M. Leclerc, A. J. Heeger, *Adv. Mater.* **2010**, *22*, 1253–1257.

[11] J. W. Kingsley, P. P. Marchisio, H. Yi, A. Iraqi, C. J. Kinane, S. Langridge, R. L. Thompson, A. J. Cadby, A. J. Pearson, D. G. Lidzey, R. A. L. Jones, A. J. Parnell, *Sci. Rep.* **2014**, *4*, 5286.

[12] The narrow feature at about 345 mT does not belong to the triplet signal and has therefore been neglected in the simulations.

[13] N. Hirota, S. Yamauchi, *J. Photochem. Photobiol. C* **2003**, *4*, 109–124.

[14] Z. M. Beiley, E. T. Hoke, R. Noriega, J. Dacuña, G. F. Burkhard, J. A. Bartelt, A. Salleo, M. F. Toney, M. D. McGehee, *Adv. Energy Mater.* **2011**, *1*, 954 – 962.

[15] X. Lu, H. Hlaing, D. S. Germack, J. Peet, W. H. Jo, D. Andrienko, K. Kremer, B. M. Ocko, *Nat. Commun.* **2011**, *3*, 795.

[16] M. Brinkmann, *J. Polym. Sci. Part B* **2011**, *49*, 1218 – 1233.

[17] A. J. Stone, *Mol. Phys.* **1964**, *7*, 311 – 316.

[18] S. Cambré, J. De Ceuster, E. Goovaerts, A. Bouwen, H. Detert, *Appl. Magn. Reson.* **2007**, *31*, 343 – 355.

[19] a) C. J. Brabec, M. Heeney, I. McCulloch, J. Nelson, *Chem. Soc. Rev.* **2011**, *40*, 1185 – 1199; b) N. E. Jackson, B. M. Savoie, T. J. Marks, L. X. Chen, M. A. Ratner, *J. Phys. Chem. Lett.* **2015**, *6*, 77 – 84.

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