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Effect of the Fibrillar Microstructure on the Efficiency of High Molecular Weight Diketopyrrolopyrrole-Based Polymer Solar Cells

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Bulk heterojunction polymer solar cells based on conjugated polymers as electron donor and fullerene derivatives as electron acceptor have been extensively investigated in the last decade and power conversion efficiencies (PCEs) reached up to 9.2% for single laver absorbers^[1] and 10.6% for tandem cells.^[2] In developing more efficient conjugated materials for solar cells, several polymer semiconductors have been synthesized in which alternating electron-rich and electron-deficient conjugated units are used to control the energy levels and optical band gap.^[3] Moreover, a high charge carrier mobility is advantageous for a successful material.^[4-6] High mobilities are achieved for materials with three-dimensional order that exhibit semicrystalline film morphologies. Recently, it is becoming increasingly clear that several different structural and molecular parameters are crucial ingredients for obtaining high PCEs in polymer solar cells.^[7] Creating a rigid conjugated backbone to enhance crystallinity and charge transport,^[8-10] introducing solubilizing side chains,^[11] improving molecular weight,^[12–14] and forming a micro-phase separation in bulk heterojunction films with the fullerene acceptor,^[15,16] all seem required to approach the intrinsic limits of energy conversion efficiencies in polymer solar cells too.^[17] This makes designing and synthesizing of superior materials a challenging task for which accurate guidelines are yet to be determined.

The rigid backbone of conjugated polymers and their characteristic feature to aggregate via π - π stacking impart a reduced solubility on these materials in common organic solvents. By introducing alkyl chains the solubility is increased, but the electrically insulating side chains influence charge transport, aggregation behavior, and the bulk heterojunction morphology when blending the polymer with a fullerene derivative in the photoactive layer of a solar cell.^[18–23] It is well established that the solubilizing side chains play a crucial role in forming the phase separation and bulk heterojunction morphology of conjugated polymer – fullerene blends,^[24,25] affecting exciton diffusion, charge dissociation, and charge transport. Even though accurate design rules for the optimal morphology are elusive,

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DOI: 10.1002/adma.201304360

micro-phase separation with domain sizes on the order of 10 nm seems to be beneficial. Control of the domain size can possibly be obtained by adjusting the solubilizing side chains in combination with processing conditions. Short side chains reduce solubility and increase the tendency to crystallize. On the other hand, longer side chains enhance solubility and create more disorder, but –in contrast– also allow achieving high molecular weights during synthesis, which also can lead to improved aggregation.^[14,26] Hence, the optimal length of side chains is not a simple choice and likely needs to be optimized for each specific conjugated backbone to achieve the best performance.

In the past five years conjugated push-pull polymers that use diketopyrrolopyrrole (DPP) unit as electron withdrawing unit have emerged as promising semiconductors for application in field-effect transistors^[27] and polymer solar cells.^[28] DPPbased conjugated polymers with side chains such as ethylhexyl (EH),^[29] butyloctyl (BO),^[30–32] hexyldecyl (HD),^[14,33,34] octyldodecyl (OD),^[16,35–37] and linear alkyl chains^[38] have been applied in solar cells with PCEs up to 8%.^[39] To obtain more insight into the effect of the side chains on the performance of organic solar cells we compare PDPPTPT polymers with HD, OD, and DT (decyltetradecyl) side chains of different length (Figure 1). The synthesis of the polymers has been optimized to achieve high molecular weights.^[39] The polymers were applied in bulk heterojunction solar cells with [70]PCBM ([6,6]-phenyl-C₇₁-butyric acid methyl ester) as acceptor, and provide PCEs ranging from 3.2% to 7.4%. We will show that the differences in PCE can be directly related to the microstructure of the bulk heterojunction as determined by transmission electron microscopy (TEM). More specifically the external quantum efficiency and photovoltaic performance correlate with the width of the long fibrils that form in blends of the PDPPTPT polymers with [70]PCBM. For fibrils that are significantly wider than ~10 nm, reduced exciton dissociation into free charges limits the performance, because not all excitons diffuse to the interface with [70]PCBM. Steady state and time-resolved fluorescence spectroscopy support this conclusion. The results demonstrate that in designing conjugated polymers for polymer solar cells, the nature of the solubilizing side chains is a crucial parameter.

The three PDPPTPT polymers were prepared by Suzuki polymerization using a catalyst system based on Pd₂(dba)₃ as source of palladium with PPh₃ as ligand (See Supporting Information for details). The molecular weight of the polymers was determined by gel permeation chromatography (GPC) using *o*-DCB as eluent at 80 °C and a low polymer concentration of 0.06 mg www.advmat.de www.MaterialsViews.com C_6H_{13} C_8H_{17} C10H21 C₁₂H₂₅ ·C₁₀H₂₁ C8H17 ć Ć C₈H HD-PDPPTPT **OD-PDPPTPT** DT-PDPPTPT Limited solubility Good solubility

Figure 1. PDPPTPT semiconducting polymers described in this work.

mL⁻¹ to reduce aggregation (Supporting Information, Figure S1). The resulting molecular weights are $M_n = 72.0$ kg mol⁻¹ for HD, $M_n = 139.6$ kg mol⁻¹ for OD, and 89.2 kg mol⁻¹ for DT (**Table 1**). The longer DT side chains impart good solubility on DT-PDPPTPT in chloroform, where as HD-PDPPTPT and OD-PDPPTPT are much more difficult to dissolve.

The electron withdrawing character of the DPP unit results in a strong push-pull system and shifts the optical absorption of the polymers into the near-infrared region. The absorption spectra of the three PDPPTPT polymers are virtually identical (Figure S2) and the optical band gap is 1.52 eV. The charge carrier mobility has been determined in field-effect transistors (FET) with a bottom-contact bottom-gate configuration and a passivated SiO₂ gate dielectric. The three PDPPTPT polymers provide very similar saturated mobilities of $\mu \ge 10^{-3}$ cm² V⁻¹ s⁻¹ for holes and for electrons (Table S1).

The PDPPTPT polymers were blended with [70]PCBM and used as active layer in solar cells with a transparent ITO/ PEDOT:PSS front contact and a reflective LiF/Al back contact. Several device and processing parameters such as the polymer to [70]PCBM weight ratio, the active layer thickness, the processing solvent, and the processing additive (1,8-diiodooctane (DIO) or o-DCB) concentration were carefully optimized to ensure that maximum photovoltaic performance was obtained for each polymer. The optimized processing conditions and layer thicknesses are collected in Table 1 together with the solar cell characteristics. The PCEs vary widely from 3.2% to 7.4%. The current density – voltage (J-V) characteristics and external quantum efficiency (EQE) are shown in Figure 2. The short circuit current (J_{sc}) and EQE clearly drop when the length of the side chains is increased from HD via OD to DT (Figure 2, Table 1). The PCE drops dramatically from 7.4% for HD-PDPPTPT, via 5.7% for OD-PDPPTPT, to 3.2% for DT-PDPPTPT. The results suggest that when obtaining high molecular weights, it remains important to approach the solubility limit of the polymers to achieve the best PCEs. We investigated the possibility to further reduce the side chain length below HD but BO-PDPPTPT was found to be a completely insoluble polymer. The BO side chains are too short to combine high molecular weight and sufficient solubility, suggesting that HD-PDPPTPT is a very close to optimal combination of side chain length for the PDPPTPT backbone.

To better understand the origin of the differences in photocurrent and PCE, the morphology of active layers was examined by bright field TEM (**Figure 3**). TEM reveals a fibrillar structure for each of the blends. The widths of the fibrils are distinctly different and increase, going from HD, via OD, to DT side chains. On close inspection lattice fringes can be seen in some of the fibrils, indicating that the fibrils represent crystalline polymer aggregates (Figure 3). From the images shown in Figure 3 it is possible to infer *d*-spacings of 1.85, 1.94, and 2.24 nm for the lamellar distance in the fibrillar crystals of HD-, OD-, and DT-PDPPTPT.

In **Figure 4** we plotted the EQE at 750 nm (corresponding to the polymer absorption) versus the average fibril width obtained from the TEM images. Despite the limited number of data points, this graph strongly suggests that wider crystalline fibrils limit charge generation. In the Supporting Information we show the solar cell and TEM data obtained for two related HD-PDPP3T and DT-PDPP3T polymers blended with [70]PCBM that are fully consistent with the results shown in Figure 4.

The relation between EQE and fibril width can be explained by exciton diffusion limiting the charge generation, which is expected when the fibril width becomes larger than the exciton

Table 1. Characteristics of Optimized Solar Cells of the PDPPTPT Polymers with [70]PCBM.

Polymer	M _n ª [kg mol ⁻¹]	$M_{ m w}^{ m a}$ [kg mol ⁻¹]	PDI	E _g ^{film} [eV]	Cosolvent	<i>d</i> [nm]	\int_{sc}^{b} [mA cm ⁻²]	V _{oc} [V]	FF	PCE ^c [%]
HD-PDPPTPT ^c	72.0	142.7	1.98	1.52	o-DCB 6%	115	14.0	0.80	0.67	7.4
OD-PDPPTPT ^c	139.6	441.7	3.16	1.52	DIO 2.5%	100	11.9	0.79	0.60	5.7
DT-PDPPTPT ^c	89.2	215.6	2.42	1.52	DIO 5%	100	6.6	0.81	0.59	3.2

^aDetermined with GPC at 80 °C using *o*-DCB as the eluent; ^b J_{sc} was calculated by integrating the EQE spectrum with the AM1.5G spectrum; ^c Weight ratio of the polymers to [70]PCBM is 1:2.



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Figure 2. (a) J-V curves and (b) EQE of the optimized PDPPTPT:[70]PCBM (1:2) solar cells for the polymers with HD, OD, or DT side chains.

diffusion length. Typical exciton diffusion lengths for conjugated polymers are a few nanometers,^[40] and hence wider fibrils may negatively affect the percentage of excitons that reach the interface with the fullerene where charge generation occurs. Figure 2a shows that at negative bias the photocurrent remains almost constant. This shows that the electrical field does not significantly enhance charge generation or charge collection and is consistent with the suggestion that the devices are limited by exciton diffusion.

To verify this hypothesis we studied the fluorescence quenching of the three PDPPTPT polymers when mixed with [70]PCBM. **Figure 5** shows the corresponding steady state fluorescence spectra recorded with selective excitation of PDPPTPT at 740 nm. Figure 5 corroborates that the PDPTPT



Figure 3. Bright field TEM images of the optimized PDPPTPT:[70]PCBM blends for HD, OD, and DT side chains. (a,b,c) Image size: $1.2 \times 1.2 \,\mu$ m². The insets give the average width of the fibrils. (d,e,f) Image size: $225 \times 225 \,\text{nm}^2$. The insets give the *d* spacings obtained from the images.

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Figure 4. Plot of the EQE at 750 nm of PDPPTPT:[70]PCBM solar cells (Figure 2b) for HD, OD, and DT side chains versus the average fibril width obtained from bright field TEM (Figure 3).

fluorescence quenching is significantly larger for the polymer with the short HD side chains than for the polymer with the long DT side chains. Fluorescence quenching factors (Q) in blends of PDPPTPT with [70]PCBM, determined after correcting for small differences in optical densities, are 4.5 for HD, 2.0 for OD, and 1.8 for DT side chains. A stronger fluorescence quenching matches with higher EQE in Figure 2b and the results support the conclusion from TEM and EQE that in narrow fibrils a larger fraction of the excitons forms charges than for wider fibrils. Single photon counting time-resolved fluorescence experiments were performed to obtain further quantification of the fluorescence quenching (Figure S3). For the pristine PDPPTPT polymers we find fast, essentially mono-exponential, decays with short lifetimes: 66 ps (HD), 62 ps (OD), and 38 ps (DT), close to the width of the instrument response function (IRF) (~30 ps). The transient fluorescence traces of the blends are multi-exponential with a fast (~30 ps) component in each case, but also contain a contribution from a longer-lived (~450 ps) [70]PCBM emission. Excitation is restricted to 400 nm in the set-up and not selective for the polymer. The time resolved data support exciton diffusion lim-

iting the dissociation of photoexcitations on the polymer into charge carriers at the interface of the fibril with the fullerene phase. Because the measured exciton lifetimes are close to the instrument response, detailed quantitative analysis of the decay data is not warranted. The data are, however, consistent with the observed steady state quenching Q (Figure 5) because for each blend the expected lifetime ($\tau_{\text{blend}} = \tau_{\text{polymer}}/Q$) is equal or below the width of the IRF.

It is possible to relate chemical structure to performance. The main idea that emerges from this work is that short side chains and high molecular weights are beneficial for providing high efficiencies, because the associated reduced solubility leads to narrow polymer fibers that sustain efficient exciton dissociation. For HD-PDPPTPT with shortest side chains (C6, C10) and $M_{\rm n} = 72.0 \text{ kg mol}^{-1}$ and the fibers are narrow (9 nm). Going to OD-PDPPTPT, the side chains (C8, C12) are longer, but also M_n = 139.6 kg mol⁻¹ increases. The first effect increases the solubility, but the second decreases the solubility and as a result the fibers of OD-PDPPTPT are similar in width (12 nm) to those of HD-PDPPTPT. The small increase shows that the effect of the side chains outweighs that of the molecular weight. Finally, for DT-PDPPTPT the side chains are the longest (C10, C14) and the molecular weight decreases to $M_n = 89.2$ kg mol⁻¹. Both effects lead to better solubility and to wider fibrils (30 nm).

In conclusion, for high molecular weight PDPPTPT the PCE can be increased from ~3.2% to 7.4% in blends with [70]PCBM by decreasing the length of the solubilizing side chains from decyltetradecyl, via octyldodecyl, to hexyldecyl. The polymers form an extended semicrystalline fibrillar network in blends with [70]PCBM and the width of the fibrils correlates with the external quantum efficiency of photon-to-electron conversion. Blends with narrow (≤12 nm) fibrils, in which excitons are more likely to diffuse to the [70]PCBM interface afford much higher external quantum efficiencies and provide improved PCEs than blends with wider fibrils. Photoluminescence quenching studies provide qualitative support for this mechanism in which the performance is limited by exciton dissociation. The results demonstrate that tuning the length of the side chains of conjugated polymers is critical for achieving high photovoltaic response. The main reason for this is that the side chains sig-

Figure 5. Photoluminescence spectra of the PDPPTPT, [70]PCBM, and PDPPTPT:[70]PCBM blends with photoexcitation at 740 nm for polymers with (a) HD, (b) OD, and (c) DT side chains. The HD-PDPPTPT:[70]blend shows larger photoluminescence quenching compared to the other two.

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nificantly affect the morphology that is formed when casting the blend films.

Experimental Section

Photovoltaic devices were made by spin coating poly(ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (Clevios P, VP Al 4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (14 Ω per square) (Naranjo Substrates). The photoactive layer were deposited by spin coating a chloroform solution containing the polymers and [70]PCBM with different ratio and the appropriate amount of 1,8-diiodooctane (DIO) or o-DCB. LiF (1 nm) and Al (100 nm) were deposited by vacuum evaporation at $\sim 2 \times 10^{-7}$ mbar as the back electrode. The active area of the cells was 0.09 or 0.16 cm² and no size dependence was found between these two dimensions. I-V characteristics were measured under ~100 mW cm⁻² white light from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB 120 daylight filter, using a Keithley 2400 source meter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The spectral response was measured under simulated 1 sun operation conditions using bias light from a 532 nm solid state laser (Edmund Optics). Light from a 50 W tungsten halogen lamp (Osram64610) was used as probe light and modulated with a mechanical chopper before passing the monochromator (Oriel, Cornerstone 130) to select the wavelength. The response was recorded as the voltage over a 50 resistance, using a lock-in amplifier (Stanford Research Systems SR 830). A calibrated Si cell was used as reference. The device was kept behind a quartz window in a nitrogen filled container. The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak 150 profilometer. TEM was performed on a Tecnai G^2 Sphera TEM (FEI) operated at 200 kV.

Steady state fluorescence spectra were recorded at room temperature using an Edinburgh Instruments FLSP920 double-monochromator luminescence spectrometer equipped with a nitrogen-cooled near-IR sensitive photomultiplier (Hamamatsu). Blend films were cast following the optimized procedures used for the solar cells and had a thickness of about 100 nm. For films of the pure polymers, the same polymer concentration and spin coating speed were used to obtain films with similar optical density at the absorption maximum of the polymer. All films were put into a high vacuum (2×10^{-8} mbar) chamber overnight to remove the possible solvent such as DIO.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

We thank Ralf Bovee for GPC analysis. The work was performed in the framework of the Largecells and X10D projects that received funding from the European Commission's Seventh Framework Programme (Grant Agreement No. 261936 and No. 287818). The work was further supported by the "Europees Fonds voor Regionale Ontwikkeling" (EFRO) in the Interreg IV-A project "Organext". The research forms part of the Solliance OPV programme and has received funding from the Ministry of Education, Culture and Science (Gravity program 024.001.035).

Received: August 30, 2013 Revised: October 1, 2013

- Revised: October 1, 2013
- Published online: November 29, 2013

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