On the Effect of Prevalent Carbazole Homocoupling Defects on the Photovoltaic Performance of PCDTBT:PC71BM Solar Cells

Florian Lombeck, Hartmut Komber, Daniele Fazzi, Diego Nava, Jochen Kuhlmann, Dominik Stegerer, Karen Strassel, Josef Brandt, Amaia Diaz de Zerio Mendaza, Christian Müller, Walter Thiel, Mario Caironi, Richard Friend, and Michael Sommer*

The photophysical properties and solar cell performance of the classical donor–acceptor copolymer PCDTBT (poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)]) in relation to unintentionally formed main chain defects are investigated. Carbazole–carbazole homocouplings (Cbz hc) are found to significant extent in PCDTBT made with a variety of Suzuki polycondensation conditions. Cbz hc vary between 0 and 8 mol% depending on the synthetic protocol used, and are quantified by detailed nuclear magnetic resonance spectroscopy including model compounds, which allows to establish a calibration curve from optical spectroscopy. The results are corroborated by extended time-dependent density functional theory investigations on the structural, electronic, and optical properties of regularly alternating and homocoupled chains. The photovoltaic properties of PCDTBT:fullerene blend solar cells significantly depend on the Cbz hc content for constant molecular weight, whereby an increasing amount of Cbz hc leads to strongly decreased short circuit currents \( J_{SC} \). With increasing Cbz hc content, \( J_{SC} \) decreases more strongly than the intensity of the low energy absorption band, suggesting that small losses in absorption cannot explain the decrease in \( J_{SC} \) alone, rather than combined effects of a more localized LUMO level on the TBT unit and lower hole mobilities found in highly defective samples. Homocoupling-free PCDTBT with optimized molecular weight yields the highest efficiency up to 7.2% without extensive optimization.

1. Introduction

Conjugated polymers are a class of extensively investigated \( \pi \)-conjugated materials suitable for a multitude of applications ranging from, e.g., photovoltaics,[1] field-effect transistors,[2] light-emitting diodes[3] and memory devices[4] to sensors and thermoelectric generators.[5] Within the last decades, an overwhelmingly large number of different building blocks have been used to construct numerous conjugated polymers with pre-selected and fine-tuned opto-electronic properties.[6,7] However, while structural diversity of conjugated materials is continuously broadening, the synthetic methods employed are often very similar. In most cases, transition metal-catalyzed polycondensation techniques based on two symmetric monomers are used, which, in the ideal case, lead to strictly alternating sequences. Therefore, when drawing the repeat unit of a conjugated polymer on paper, an alternating structure is implicitly assumed. However, it is also known that besides typical cross-coupling
products other products can form due to homocoupling (hc) reactions, depending on a variety of reaction parameters. The reason this may be a decisive factor when synthesizing conjugated polymers for organic electronics is that small degrees of polymerization are often obtained and, hence, any deviation from an alternating chain structure constitutes a non-negligible fraction of the chain, which consequently exhibits altered optoelectronic properties. The most common possibility for main chain electronic defects arises from hc reactions as seen with Kumada,[13] Suzuki,[14–16] and direct arylation polycondensations.[17–20] For Stille polycondensations, homocoupling reactions have been claimed to be present as well.[21,22] If occurring during polycondensation, covalent incorporation into the conjugated polymer backbone takes place and the resulting defects cannot be removed subsequently. Homocoupling reactions in Suzuki small molecule[23] and polycondensation reactions are assumed to be caused by the coupling of polymer chains having boronic ester end groups as shown by early work of Heitz et al. and by us recently.[14,24] Interestingly, the impact of hc and thus main chain defects on the optoelectronic performance of conjugated materials remains largely unknown. Hendriks et al. recently reported the detrimental effect of intentionally homocoupled dithienyl-diketopyrrolopyrrole (DPP) units in DPP copolymers on their solar cell performance. In this case, DPP-DPP hc were shown to be present on the basis of explicitly designed defect comonomers and UV–vis spectroscopy experiments.[15] On the basis of these results there is strong indication that hc defects may be present in many other systems as well. As quantification of homocouplings is challenging, both their extent as well as their effect on optoelectronic properties is largely unknown. Thus, the investigation of defect–function relationships appears to be crucially important for further improving device performance and to ensure comparability and reproducibility of device performance.

Here, we investigate the impact of carbazole–carbazole homocouplings (Cbz hc) present in the often used conjugated polymer poly(N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)) (PCDTBT) on its solar cell performance in blend films with PC71BM as acceptor material. Using PCDTBT:PC71BM blends, power conversion efficiencies (PCE) up to ≈7% and internal quantum efficiencies approaching 100% have been reported.[21–25] At the same time, a broad range of PCE values from 3.5% to 7% can be found in the literature.[26] PCDTBT additionally offers excellent stability and operational lifetime of photovoltaic devices.[26,27] Using model dimers and PCDTBT with intentionally introduced Cbz hc, we first identify the 1H NMR chemical shifts of both TBD as well as Cbz hc sequences, and subsequently quantify their occurrence for a variety of different Suzuki polycondensation protocols. While we find Cbz hc to occur under almost every catalytic condition used, TBD homocouplings are seldom found, and, if at all, with very low intensity. From 1H NMR and UV–vis spectroscopy a calibration curve is established from which the Cbz hc content can simply be determined. Time-dependent density functional theory (TDDFT) calculations further support the experimental findings. Changes in the UV–vis band intensities can be reproduced upon the insertion of hc defects, and effects of hc defects on intramolecular hole reorganization energies are small. Finally, we show that the photovoltaic performance of PCDTBT:PC71BM blends substantially deteriorates with increasing content of Cbz hc, which can partially be ascribed to reduced absorption by the charge-transfer band, and eventually to a more localized LUMO level on the TBD unit. As PCDTBT synthesis reported in the literature is mostly performed under conditions leading to defective materials, this work provides an explanation why comparability of device data is generally challenging. For future studies main chain electronic defects in conjugated polymers arising from homocoupling reactions must be considered as an additional parameter next to molecular weight (MW) and dispersity.

2. Results and Discussion
2.1. Synthesis and Materials

All synthetic procedures are described in detail in the Supporting Information. The dimer models are abbreviated as Cbz-Cbz, TBD-TBD, and Cbz-TBD; for chemical structures see the Supporting Information. PCDTBT is prepared by varying Suzuki polycondensation (SPO) protocols and is numbered as PCDTBT 1–11. Molecular weights are determined by high-temperature size exclusion chromatography (HT-SEC) in 1,2,4-trichlorobenzene at 150 °C and, to ensure compatibility with the majority of existing literature, given relative to polystyrene standards (Table 1). We used viscosity detection to extract the Mark–Houwink parameters K and α and thus attempted to establish a universal calibration, and found that molecular weights obtained from universal calibration were too low when compared to qualitative values from 1H NMR (Table S1, Supporting Information). Table 1 also collects all important information of the PCDTBT samples used. Typical synthesis procedures are denoted as conditions (i–v) and are described in Scheme 1a as well as in detail in the Supporting Information. Catalysts were selected according to their appearance in the literature, air stability, and activity. Generally, it was found that the type of Pd precursor has the largest influence on the amount of Cbz homocouplings, with Pd(PPh3)4 being the only catalyst that enabled the synthesis of homocoupling-free PCDTBT 1, 7, and 11 with different molecular weight. All other catalytic systems, including Pd(dbaz)3/ phosphine, third generation Buchwald catalyst G3/phosphine and G2[p-toly1]2[28] led to varying Cbz hc contents of 2–8 mol% (PCDTBT 2–5, 8, 9). Model copolymers PCDTBT 6 and 10 with intentionally introduced carbazole homocoupling defects were made by incorporating 10 mol% of an asymmetric carbazole comonomer leading to Cbz dimer sequences (Scheme 1b). Importantly, as molecular weight affects photovoltaic performance of PCDTBT:PC71BM blends as well,[21] two series of PCDTBT with similar weight average molecular weights of $M_w = 30$ and 60 kDa, obtained as chloroform and chlorobenzene fractions, respectively, but varying defect concentrations were selected for further analysis (Table 1). We prefer to use $M_w$ rather than $M_n$ values for comparison as the latter ones are much more sensitive to small variations in oligomer intensity. Usage of different molecular weight is highly important to elucidate effects of varying chain lengths. This is important especially for conjugated polymers where the degrees of polymerization are generally low. Thus, PCDTBT
with a similar \( M_w \) of 30 kDa and PCDTBT 7–10 with similar \( M_w \) of 60 kDa were used for the investigation of defect–function relationships.

### 2.2. Identification and Quantification of Cbz and TBT Homocouplings

Recently, we have shown Cbz hc to occur during the synthesis of PCDTBT and hexyl-substituted PCDTBT derivatives by direct arylation polycondensation and SPC.[16,17] Here, we quantify the signals of Cbz hc in PCDTBT in relation to a variety of SPC conditions. Additionally, we also elucidated whether TBT homocouplings formed with measurable content. To this end, we used the \(^1\)H NMR data of the dimer TBT-TBT to estimate the chemical shifts of TBT hc in a Cbz-TBT-TBT-Cbz sequence taking into account chemical shift effects of neighboring Cbz units (for a detailed analysis see the Supporting Information). The thiophene protons of the central T-T unit showed up as doublets with a coupling constant of \( \approx 3.2 \) Hz at \( \approx 7.44 \) and \( \approx 8.16 \) ppm. Thus, for the identification of possible TBT-TBT sequences in PCDTBT, the 7.44 ppm signal appeared ideal, as overlap with backbone signals is not present (Figure S2, Supporting Information). Unfortunately, protonated carbazole end...

| #  | Method(a) | Cat                        | \( M_n/M_w \)(b) [kDa] | Cbz hc(c) | Ratio \( I_{ee}/I_{en} \)(d) |
|----|-----------|----------------------------|------------------------|-----------|---------------------------|
| 1  | i\(^1\)   | Pd[PPh\(_3\)]\(_4\)       | CF: 8/32               | 0         | CF: 1.195                 |
| 2  | ii\(^1\)  | Pd\(_2\)dba\(_3\) SPHOS   | CF: 10/33              | 2.4       | CF: 1.149                 |
| 3  | iii\(^1\) | Pd\(_2\)dba\(_3\) SPHOS   | CF: 12/33              | 3.6       | CF: 1.113                 |
| 4  | iv\(^1\)  | Pd\(_2\)dba\(_3\) SPHOS   | CF: 7/35               | 6.0       | CF: 1.064                 |
| 5  | v\(^1\)   | Pd\(_2\)G\(_3\) SPHOS     | CF: 10/30              | 8.0       | CF: 1.024                 |
| 6  | vi\(^1\)  | Pd\(_2\)dba\(_3\) SPHOS   | CF: 12/43              | 10.0      | CF: 0.985                 |
| 7  | i\(^1\)   | Pd[PPh\(_3\)]\(_4\)       | CB: 23/72              | 0         | CB: 1.251                 |
| 8  | iii\(^1\) | Pd\(_2\)dba\(_3\) SPHOS   | CF: 15/48              | 2.5       | CF: 1.089                 |
| 9  | iv\(^1\)  | Pd\(_2\)dba\(_3\) P(o-tol)\(_3\) | CB: 28/58  | 4.0       | CF: 1.158                 |
| 10 | v\(^1\)   | Pd\(_2\)dba\(_3\) SPHOS   | CB: 21/52              | 10.0      | CF: 0.975                 |
| 11 | i\(^1\)   | Pd[PPh\(_3\)]\(_4\)       | CB: 25/81              | 0         | CB: 1.279                 |

\(^a\)For synthetic methods see caption of Scheme 1; \(^b\)Obtained from high-temperature SEC in TCB at 150 °C; \(^c\)From \(^1\)H NMR spectroscopy; \(^d\)Ratio of absorption bands in chlorobenzene at 0.02 mg mL\(^{-1}\); \(^e\)90 °C reaction temperature; \(^f\)80 °C reaction temperature. CF and CB indicate chloroform and chlorobenzene fractions, respectively.

**Table 1.** Overview of PCDTBT samples used in this study.  

**Scheme 1.** a) Synthesis of PCDTBT under varying Suzuki polycondensation conditions and b) with intentionally introduced Cbz hc defects. Reaction conditions: (i) \( X = \text{Br}, \text{Pd(PPh}_3\text{)}_4\), 2 \( \mu\) K\(_2\)CO\(_3\), toluene, 90 °C, 2 d; (ii) \( X = \text{Br}, \text{Pd}_2\text{dba}_3/\text{phosphine (SPHOS or P(o-tol)_3)}, 2 \mu\) K\(_2\)CO\(_3\), toluene, 90 °C, 2 d, (iii) \( X = \text{Cl}, \text{Pd}_2\text{dba}_3/\text{SPHOS}, 2 \mu\) K\(_2\)CO\(_3\), toluene, 80 °C, 2 d; (iv) \( X = \text{Br}, \text{Pd}_2\text{G}_3\)/ SPHOS, 2 \( \mu\) K\(_2\)CO\(_3\), toluene, 90 °C, 20 min, (v) \( X = \text{Br}, \text{PdG}_2(o\text{-toly})_3\)P, 2 \( \mu\) K\(_2\)CO\(_3\), toluene, 90 °C, 20 min; and (vi) \( \text{Pd}_2\text{dba}_3/\text{SPHOS, 2 \mu\text{K}_2\text{CO}_3, toluene, 3 h, 90 °C, microwave-assisted heating.} \)
groups (Cbz–H) arising from protio-deborylation resulted in a triplet at this same position with a coupling constant of 7.5 Hz.\(^{[17]}\) In principle, the two different coupling constants allowed to distinguish between TBT hc and Cbz–H end groups. Careful inspection of all PCDTBT spectra unequivocally proved the presence of TBT hc only for PCDTBT 8 as also confirmed by correlation peaks between signals at 7.47 and 8.18 ppm in its TOCSY spectrum (see Figure S3, Supporting Information). However, the TBT hc content of PCDTBT 8 was very low and hence could not reliably be quantified. While TBT hc cannot be entirely ruled out for other samples, but could, compared to the frequently and much more intensely occurring Cbz hc, be clearly neglected. Therefore, in the present study we focus on how changes in the opto-electronic properties of PCDTBT evolve for Cbz hc contents of 0–10 mol%. In order to assign the Cbz hc unit unambiguously, the \(^1\)H chemical shifts were estimated by the aforementioned model approach based on dimers Cbz-Cbz and Cbz-TBT (see the Supporting Information). To confirm these estimations, model PCDTBT 6 and 10 with intentionally introduced isolated Cbz dimer sequences mimicking the Cbz hc were prepared (Scheme 1b). Estimated and experimental \(^1\)H chemical shift values were in very good agreement. Two characteristic doublets at 8.16 and 8.23 ppm allowed quantifying the Cbz hc content, whereas the remaining four signals were overlapped by backbone signals. Similar to the definition of regioregularity of P3HT,\(^{[13]}\) we defined the Cbz hc content as the amount of Cbz-Cbz linkages divided by the total number of both Cbz-Cbz and Cbz-TBT linkages. It is reasonable to assume that the monomer feed content of 10 mol% of the asymmetric Cbz comonomer was fully incorporated into PCDTBT 6 and 10 (Scheme 1b, Table 1). Deconvolution of the 8.35–8.1 ppm region results in signal intensities for Cbz-Cbz and Cbz-TBT linkages, and indeed a Cbz hc content of 10 mol% was found for PCDTBT 10 and 11 (see the Supporting Information). As for these two entries a catalytic system giving 2%–3% un-intentional Cbz hc was used, a Cbz hc value of 12%–13% could have been expected. However, this is not confirmed by \(^1\)H NMR and might be explained by the fact that microwave heating was used, in which cases generally lower homocoupling contents were found. All other PCDTBT samples made under varying Suzuki conditions (Scheme 1a) were inspected with respect to Cbz hc and, if present, the Cbz hc content was determined by deconvolution or by comparison to deconvoluted samples (Table 1). The accuracy of both approaches depends on the line width and the content of TBT–H end groups, which also give signals in the 8.35–8.1 ppm region. As an example, Figure 1 shows high-temperature \(^1\)H NMR spectra of the two PCDTBT samples 6 and 7 with high molecular weight. PCDTBT 6 was made with intentionally introduced 10 mol% Cbz hc (Figure 1b), while PCDTBT 7 is homocoupling-free (Figure 1a). Figure S6 (Supporting Information) further shows a series of six PCDTBT samples 1–6 with very similar weight average molecular weights \(M_{w,SEC} \approx 30 \text{ kDa}\) but with varying Cbz hc content. Obviously, Pd[PPh\(_3\)]\(_4\) was the only catalyst that enabled the preparation of hc-free PCDTBT samples 1, 7, and 11 while all other catalytic systems led to Cbz hc content of 2–8 mol%. Also the commonly used combination of Pd[db] (phosphine (P(\(\sigma\)-tolyl)), and SPHOS) led to clearly visible, albeit small amounts of 2–4 mol% Cbz hc in PCDTBT 2, 3, 8, 9. Usage of the highly active Buchwald catalysts Pd\(_2\)(G3)\(_2\) and Pd\(_2\)(\(\sigma\)-tolyl)\(_3\)P enabled the synthesis of PCDTBT 4 and 5 within minutes but led to significantly increased amounts of Cbz hc between 6 and 8 mol% (Figure S6, Supporting Information).

2.3. Steady-State Spectroscopy and the Establishment of a Calibration Curve

Having identified the fraction of homocoupled Cbz units for a variety of SPC conditions, we selected samples with constant molecular weight but varying Cbz hc content for further analysis of opto-electronic properties. Two series of samples, PCDTBT 1–6 with \(M_w \approx 30 \text{ kDa}\) and PCDTBT 7–10 with \(M_w \approx 60 \text{ kDa}\) both having Cbz hc contents of 0–10 mol% were chosen and investigated by steady-state absorption, photoluminescence spectroscopy, and HOMO energy level determination via ultraviolet photoelectron spectroscopy (UPS) (Figure 2 and Figures S1-7 and S1-8). UV–vis absorption in chlorobenzene showed a clear reduction of the low-energy band (CT-like transition, see assignment next paragraph) with increasing Cbz hc content (Figure 2a). An increasing amount of Cbz hc can correlate with a decreasing amount of TBT units in the chain, which can explain the linear decreases of the CT band cross section. Thus, correlating solution absorption properties with the content of Cbz hc appeared to be reasonable. Plotting the intensity ratio of the low and high-energy absorption bands \((I_{low}/I_{high})\) in the solution spectra versus mol% Cbz hc gave a straight line that follows \(I_{low}/I_{high} = -0.02463 \text{ mol}\% \text{ Cbz hc} + 1.2037\) (Figure 2b). For molecular weights (MWs) higher than \(M_w \approx 30 \text{ kDa}\), the data points lie above this straight line, indicating that a saturation of the electronic conjugation length of PCDTBT in solution has not yet been reached (Figure 2b). From this straight line, Cbz homocoupling contents can easily be extracted for any...
sample without measuring and evaluating high-temperature NMR measurements, and effects of molecular weight can be accounted for as well. The photoluminescence quantum efficiency (PLQE) in solution, excited at 532 nm, increased with Cbz hc, indicating that the perfectly alternating chain exhibits the lowest PLQE values (Figure 2b). This is fully congruent with statistical TBT copolymers which show increased PL values if the TBT unit is used as increasingly diluted comonomer. The HOMO energy level determined by UPS is found to slightly decrease with increasing Cbz hc, lying between $\pm 0.04$ eV for defect-free PCDTBT 1 and $\pm 0.15$ eV for PCDTBT 6 having 10 mol% Cbz hc (Figures SI-7 and SI-8).

### 2.4. DFT Calculations

To get insight into the experimental photophysical properties, DFT and TD-DFT calculations were performed. The polymers are represented as finite size oligomers featuring four monomeric units. The alternating chain is denoted as (Cbz-TBT)$_4$, and the Cbz-Cbz and the TBT-TBT cases as (TBT-Cbz-Cbz-TBT-Cbz-TBT-Cbz-TBT) and (Cbz-TBT-Cbz-TBT-Cbz-TBT-Cbz), respectively. Although the TBT homocoupling defect is experimentally observed with very minor content, it is considered here to explore the impact of such kind of defects. This might be of interest as halide–halide homocoupling reactions have been observed recently, and hence should be generally considered. Two DFT functionals were employed, the hybrid B3LYP-D3 and the long-range separated LC-BLYP-D3 (range separated parameter optimized at $\mu = 0.21$) with inclusion of Grimme’s dispersion corrections (D3) and the 6-311G* basis set. Both gas-phase and solvent-dependent (conductor polarizable continuum model CPCM with a dielectric constant for chlorobenzene of 5.6968) calculations were performed. Charged species (+1) were fully optimized as well, and intramolecular hole reorganization energies for the three cases (alternating, Cbz-Cbz, and TBT-TBT) were computed at the LC-BLYP level of theory. Because of their best match with the experimental data, we report the CPCM-LC-BLYP results here. All other computational results are given in the Supporting Information. All calculations were performed using Gaussian 09 revision D.01.

Figure 3 shows the frontier molecular orbital isosurfaces (HOMO and LUMO) for the three cases. The HOMO topography is not affected by the hc defect, preserving its delocalized $\pi$-character over the oligomer length. The LUMO spatial distribution, intrinsically localized on the TBT unit (see alternating case), is however affected by the hc defect. In case of Cbz hc, the LUMO is localized on single TBT units, while for TBT hc it is delocalized over the two adjacent TBT units (Figure 3). Consequently, the molecular orbital energies (see the Supporting Information) slightly vary for the HOMO ($\pm 0.04$ eV), but are more sensitive for the LUMO ($\pm 0.15$ eV) when going from the alternating to the Cbz-Cbz and TBT-TBT hc cases. Figure 4
2.5. Photovoltaic Performance

Having identified and quantified Cbz homocoupling contents of various PCDTBT materials together with their influence on photophysical properties, we next turn to the question inasmuch such main chain defects affect solar cell performance. Figure 4 and Table 2 show current density–voltage (J–V) and external quantum efficiency (EQE) curves. Clearly, the short circuit current $J_{SC}$ strongly decreased continuously with increasing Cbz hc content for both the 30 and 60 kDa series. The open circuit voltage remained approximately constant, in accordance with the only very slightly altered HOMO level (Figures SI-7 and SI-8). Comparing PCDTBT 1 (0% hc) and PCDTBT 6 (10% hc) within the 30 kDa series, the $J_{SC}$ almost halved from 12.15 to 6.29 mA cm$^{-2}$. Comparing PCDTBT 7 (0% hc) and PCDTBT 10 (10% hc) within the 60 kDa series, the $J_{SC}$ dropped from 13.74 to 9.91 mA cm$^{-2}$. The best performance was obtained from Cbz hc-free PCDTBT 7 with 60 kDa (highest PCE 7.17%, average 6.85%). While the shape of the J–V curves representing the 60 kDa series is similar for PCDTBT 7, 9, and 10, PCDTBT 8 exhibits an exceptionally low fill factor as well as a reduced $J_{SC}$. We attribute this observation to the TBT hc formation observed in PCDTBT 8. In addition, although not doubtlessly identified for PCDTBT 2, we speculate TBT hc to be present in this sample as well. The strong reduction in the $J_{SC}$ with increasing Cbz hc content cannot be explained by the reduced absorption of the charge-transfer band alone (see Figure S11, Supporting Information, for blend film absorption), indicating that additional factors causing the lower organic photovoltaics (OPV) performance of defective PCDTBT are likely at play. Reorganization energies obtained from DFT calculations on isolated oligomers, which can be considered as an important parameter for intramolecular charge transport, do not reveal major changes (see the Supporting Information). However, as defects can induce changes in the intermolecular charge transport properties, charge transport was carefully probed using field-effect transistor mobilities in bottom-contact top-gate geometry. We find the field-effect hole mobilities $\mu_h$ of all PCDTBT samples within one order of magnitude, on the order of $\approx 0.5 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ (Table 2 and Supporting Information). Under the same processing conditions, the $\mu_h$ 30 kDa series exhibits the highest $\mu_h$ values for samples with none or limited Cbz hc: $\mu_h = 2.87 \pm 0.24 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ and $\mu_h = 4.22 \pm 0.24 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ are obtained for PCDTBT 1 (0% Cbz hc) and PCDTBT 3 (3.6% Cbz hc), respectively. On average, lower mobilities are observed for higher Cbz hc contents, but with no continuous trend: while a significantly lower $\mu_h$ is measured for PCDTBT 4 with a Cbz hc content of 6% (0.527 $\pm$ 0.022 $\times$ 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$) and for PCDTBT 10 with 10% (0.71 $\pm$ 0.11 $\times$ 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$), $\mu_h$ is only smaller by a factor of 2 compared to the best mobility obtained for PCDTBT 5 (8% Cbz hc, 2.17 $\pm$ 0.19 $\times$ 10$^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$). Overall the FET data indicate that reasonably good transport properties are obtained in all samples, with higher mobilities achieved for low contents of Cbz hc. While a direct comparison with PCE is not attempted because of the largely different operating conditions, subtle changes in charge transport are likely to be present in solar cells made with different polymer samples. However, given the absence of a continuous trend, we speculate that hole mobility may represent just one, possibly yielding a milder effect, of a set of interacting parameters leading to drastically reduced $J_{SC}$ upon increasing defect concentration. In this context, the stronger localization of the LUMO on the TBT unit in the Cbz
hc case compared to strictly alternating structures may lead to reduced exciton dissociation, which more strongly translates into reduced short circuit currents.\[15\]

The impact of Cbz hc defects on the photovoltaic performance of PCDTBT:PCBM blends is interesting in several aspects. First of all, the highest performance can be obtained when using defect-free PCDTBT. Secondly, considering main chain electronic defects as an additional parameter leads to better comparability of results and hence to a generally deeper understanding of structure–function relationships. To test this, we compare our OPV device efficiencies reported here with those reported by Kingsley et al.\[29\] Importantly, we used exactly the same device architecture, preparation conditions and hence a comparable layer thickness of \(\approx 80\) nm. Figure S12 (Supporting Information) shows that the trend of a first increasing and then decreasing PCE with molecular weight of PCDTBT

---

**Figure 5.** Solar cells characteristics of PCDTBT:PC71 BM blends with varying Cbz hc content. a) \(J–V\) curves and b) respective external quantum efficiencies (EQE) of PCDTBT (\(M_w\) ≈ 30 kDa) 1 (0%), 2 (2.4%), 3 (3.6%), 4 (6%), 5 and 6 (10%). c) \(J–V\) curves and d) respective external quantum efficiencies of PCDTBT (\(M_w\) ≈ 60 kDa) 7 (0%), 8 (2.5%), 9 (4%), and 10 (10%).

---

**Table 2.** Overview of solar cell and OFET parameters; average values are given, characteristics of the best cell are given in brackets. n.d.: not determined.

| \(M_w\) | \# | \(J_{SC}\) [mA cm\(^{-2}\)] | \(V_{OC}\) [V] | FF | PCE [%] | \(\mu_{OFET} \times 10^{-3}\) [cm\(^2\) V\(^{-1}\) s\(^{-1}\)] |
|-------|----|-----------------|---------|-----|--------|-----------------|
| 30 kDa | 1  | 12.15 ± 0.43    | 0.86 ± 0.02 | 0.50 ± 0.02 | 5.22 ± 0.53 (5.78) | 2.87 ± 0.24 |
|       | 2  | 12.63 ± 0.48    | 0.83 ± 0.02 | 0.34 ± 0.04 | 3.56 ± 0.26 (3.79) | n.d.         |
|       | 3  | 11.05 ± 0.29    | 0.88 ± 0.02 | 0.41 ± 0.02 | 3.97 ± 0.16 (4.12) | 4.22 ± 0.41 |
|       | 4  | 9.43 ± 0.50     | 0.86 ± 0.01 | 0.50 ± 0.04 | 4.05 ± 0.28 (4.27) | 0.327 ± 0.022 |
|       | 5  | 9.75 ± 0.62 (10.37) | 0.86 ± 0.03 (0.89) | 0.37 ± 0.02 (0.38) | 3.10 ± 0.41 (3.51) | 2.17 ± 0.19 |
|       | 6  | 6.29 ± 0.68     | 0.81 ± 0.04 | 0.36 ± 0.03 | 1.83 ± 0.31 (2.05) | n.d.         |
| 60 kDa | 7  | 13.12 ± 0.62 (13.74) | 0.87 ± 0.01 (0.87) | 0.60 ± 0.02 (0.60) | 6.85 ± 0.32 (7.17) | 2.63 ± 0.42 |
|       | 8  | 11.17 ± 0.32 (11.49) | 0.88 ± 0.01 (0.88) | 0.44 ± 0.03 (0.47) | 4.38 ± 0.17 (4.75) | n.d.         |
|       | 9  | 12.78 ± 0.39 (13.17) | 0.88 ± 0.01 (0.88) | 0.53 ± 0.02 (0.55) | 6.15 ± 0.13 (6.28) | 5.30 ± 0.15 |
|       | 10 | 9.91 ± 0.26 (10.09) | 0.90 ± 0.02 (0.91) | 0.47 ± 0.02 (0.48) | 4.19 ± 0.21 (4.40) | 0.71 ± 0.11 |
| 80 kDa | 11 | 12.62 ± 0.39 (12.99) | 0.88 ± 0.02 (0.89) | 0.54 ± 0.02 (0.55) | 5.99 ± 0.36 (6.35) | n.d.         |
can be reproduced. Also in accordance with Kingsley et al., we also find the chlorobenzene fraction with $M_n = 22$ kDa to perform best. However when PCDTBT 7 ($M_n = 23$ kDa, defect-free, chlorobenzene fraction) is compared to the chlorobenzene fraction used by Kingsley et al. (made by Pd$_2$dba$_3$/P(o-tolyl)$_3$), hence likely to contain 4% of Cbz hc, a higher PCE is obtained (7.17 vs 6.15%, respectively), revealing the beneficial effect of strictly alternating PCDTBT chains on photovoltaic performance. Looking at PCDTBT 9 (chlorobenzene fraction $M_n$ 28 kDa, 4% Cbz hc) which has been made by the same reaction conditions as used by Kingsley et al., the PCE drops to 6.15%, which is in excellent agreement (see Figure S12, Supporting Information). Importantly, the highest PCE exceeding 7% is only obtained with PCDTBT samples in which molecular weight is optimized and Cbz hc defects are eliminated. We note that higher PCE values for PCDTBT:PC$_7$BM solar cells have been reported, but emphasize that the herein presented values stem from non-optimized devices made under conditions directly used from reference studies.

3. Conclusion

We have investigated the influence of carbazole homocoupling defects (Cbz hc) frequently occurring in PCDTBT samples made by Suzuki polycondensation on the resulting opt-electronic properties. Cbz hc are quantified using high-temperature NMR spectroscopy assisted by model compounds, are correlated with synthetic conditions and are finally fully eliminated to yield homocoupling-free materials. Correlation to UV–vis spectra enables a calibration curve from which the content of Cbz hc can be simply read out. Cbz hc strongly deteriorate the short circuit current and the device performance of photovoltaic cells. Interestingly, the majority of literature protocols for the synthesis of PCDTBT use conditions that lead to Cbz hc, hence the majority of PCDTBT samples used for OPV device testing may be defective as well. We believe that varying Cbz hc are one important factor responsible for poor reproducibility and comparability of different batches and results, and stress that next to molecular weight and molecular weight distribution electronic main chain defects must be considered to fully characterize, evaluate, and compare results from conjugated polymers used in organic electronic devices.

Supporting Information

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

Acknowledgements

The authors thank M. Menke for fruitful discussions, A. Konwitz (IPF Dresden) for performing the HT-NMR measurements, A. Lederer and J. Lenz for performing some of the HT-SEC measurements, A. Mårtensson (Chalmers) for help with HT-SEC measurements, and A. Hasenhindl (University of Freiburg) for additional NMR measurements. F.L., M.S., and R.F. gratefully acknowledge the EPSRC for funding. M.S. thanks the University of Freiburg (Innovationsfond Forschung) and the DFG for funding (SPP 1355). D.F. acknowledges the Alexander von Humboldt foundation for a postdoctoral research fellowship. A.D.Z.M. and C.M. thank the Swedish Research Council for funding.

Received: June 9, 2016
Revised: June 24, 2016
Published online: August 8, 2016

[1] L. Dou, J. You, Z. Hong, Z. Xu, G. Li, R. A. Street, Y. Yang, Adv. Mater. 2013, 25, 6642.
[2] H. Siringhaus, Adv. Mater. 2014, 26, 1319.
[3] L. Ying, C.-L. Ho, H. Wu, Y. Cao, W.-Y. Wong, Adv. Mater. 2014, 26, 2459.
[4] P. Heremans, G. H. Gelincik, R. Müller, K.-J. Baeg, D.-Y. Kim, Y.-Y. Noh, Chem. Mater. 2011, 23, 341.
[5] Q. Zhang, Y. Sun, W. Xu, D. Zhu, Adv. Mater. 2014, 26, 6829.
[6] Y.-J. Cheng, S.-H. Yang, C.-S. Hsu, Chem. Rev. 2009, 109, 5868.
[7] Y. He, W. Hong, Y. Li, J. Mater. Chem. C 2014, 2, 8651.
[8] K. C. Kong, C. H. Cheng, J. Am. Chem. Soc. 1991, 113, 6313.
[9] R. van Asselt, C. J. Elsevier, Organometallics 1994, 13, 1972.
[10] A. Lei, X. Zhang, Tetrahedron Lett. 2002, 43, 2525.
[11] C. Adamo, C. Amatore, I. Ciofini, A. Jutand, H. Lakmini, J. Am. Chem. Soc. 2006, 128, 6829.
[12] W. D. Miller, A. H. Fray, J. T. Quatroche, C. D. Sturgill, Org. Process Res. Dev. 2007, 11, 359.
[13] P. Kohn, S. Huettner, H. Komer, V. Senkovskyy, R. Tkachov, A. Kiriy, R. H. Friend, U. Steiner, W. T. S. Huck, J.-U. Sommer, M. Sommer, J. Am. Chem. Soc. 2012, 134, 4790.
[14] F. Koch, W. Heitz, Macromol. Chem. Phys. 1997, 198, 1531.
[15] K. H. Hendriks, W. Li, G. H. L. Heintges, G. W. P. van Puijissen, M. M. Wierk, R. A. J. Janssen, J. Am. Chem. Soc. 2014, 136, 11128.
[16] F. Lombeck, R. Matsidik, H. Komer, M. Sommer, Macromol. Rapid Commun. 2015, 36, 231.
[17] F. Lombeck, H. Komer, S. I. Gorelsky, M. Sommer, ACS Macro Lett. 2014, 3, 819.
[18] S. Kowalski, S. Allard, U. Scherf, Macromol. Rapid Commun. 2015, 36, 1061.
[19] S. Broll, F. Nübling, A. Luzio, D. Lentzas, H. Komer, M. Cairoi, M. Sommer, Macromolecules 2015, 48, 7481.
[20] A. E. Rudenko, B. C. Thompson, J. Polym. Sci., Part A: Polym. Chem. 2015, 53, 135.
[21] W. Hong, S. Chen, B. Sun, M. A. Arnould, Y. Meng, Y. Li, Chem. Sci. 2015, 6, 3225.
[22] T. Vangerven, P. Verstappen, J. Drijkoningen, W. Dierckx, S. Himmelberger, A. Salleo, D. Vanderzande, W. Maes, J. V. Manca, Chem. Mater. 2015, 27, 3726.
[23] S. H. Park, A. Roy, S. Beaufre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, Nat. Photonics 2009, 3, 297.
[24] N. Bloquin, A. Michaud, M. Leclerc, Adv. Mater. 2007, 19, 2295.
[25] S. Beaufre, M. Leclerc, J. Mater. Chem. A 2013, 1, 11097.
[26] C. H. Peters, I. T. Sachs-Quintana, J. P. Kastrop, S. Beaufre, M. Leclerc, M. D. McGehee, Adv. Energy Mater. 2011, 1, 491.
[27] W. R. Mateker, I. T. Sachs-Quintana, G. F. Burkhard, R. Checharoen, M. D. McGehee, Chem. Mater. 2015, 27, 404.
[28] N. C. Bruno, M. T. Tudge, S. L. Buchwald, Chem. Sci. 2013, 4, 916.
[29] 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.
[30] Q. Hou, Y. Xu, W. Yang, M. Yuan, J. Peng, Y. Cao, J. Mater. Chem. 2002, 12, 2887.
[31] A. Luzio, D. Fazzi, F. Nübling, R. Matsidik, A. Straub, H. Komber, E. Giussani, S. E. Watkins, M. Barbatti, W. Thiel, E. Gann, L. Thomsen, C. R. McNeill, M. Caironi, M. Sommer, Chem. Mater. 2014, 26, 6233.

[32] K. Sen, R. Crespo-Otero, O. Weingart, W. Thiel, M. Barbatti, J. Chem. Theory Comput. 2013, 9, 533.

[33] S. Grimme, S. Ehrlich, L. Goerigk, J. Comput. Chem. 2011, 32, 1456.

[34] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 2003, 24, 669.

[35] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford, CT 2009.