Homocoupling defects limit exciton diffusion in a conjugated polymer

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Copolymers such as PCDTBT (poly(N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole)) are commonly employed as donor material in bulk heterojunction solar cells. Recently, chemical defects such as homocouplings have been shown to form at the material synthesis stage, strongly reducing the short circuit current of organic photovoltaics. Here we show that carbazole homocoupling limits exciton diffusion in PCDTBT. The diffusion coefficient decreased by one order of magnitude at 10% homocoupling concentration in a film. We propose a mechanism that explains the limitation of exciton diffusion caused by high homocoupling concentrations and short chain lengths. Diffusion is limited when either chain length or homocouplings impair the effective conjugation length of the polymer chain. We expect our findings to be relevant for copolymers in general.

Keywords: exciton diffusion; organic semiconductors; photovoltaics; homocoupling; PCDTBT

I. INTRODUCTION

Exciton diffusion is crucial for organic photovoltaic devices (OPV) as singlet excitons are the primary photoexcitations in organic semiconductors. Conjugated copolymers are organic semiconductors commonly used in organic photovoltaic devices. Copolymers with donor-acceptor structure are a promising material class in organic photovoltaics. Their optoelectronic properties can be controlled by pairing different donor and acceptor subunits. Copolymer-based single-junction bulk heterojunction solar cells have recently demonstrated a record power conversion efficiency of 11.5%.¹ When considering a certain conjugated copolymer, a strictly alternating chemical structure is commonly assumed. However, this assumption has been challenged by recent literature.²,³ The copolymer PCDTBT (poly(N-9’-heptadecanyl-2,7-carbazole-alt-5,5-(4’,7’-di-2-thienyl-2’,1’,3’-benzothiadiazole))) consists of alternating carbazole (cbz) and thiophene-benzothiadiazole-thiophene (TBT) groups. The connection between its molecular and optoelectronic properties are well studied.³⁻⁸ Lombeck et al. showed that most synthesis protocols for PCDTBT lead to significant concentrations of carbazole homocoupling.³ Hendriks et al. and Lombeck et al. have demonstrated lower photocurrents in solar cells with diketopyrrolopyrrole-based copolymers and PCDTBT, respectively.²,⁵ Both studies suggested reduced exciton dissociation caused by localized levels of lowest unoccupied molecular orbitals (LUMO) as an explanation. Here, for the first time, we unravel a dependence of exciton diffusion on homocoupling density. Exemplified by a series of PCDTBT samples with varying carbazole homocoupling density and molecular weight, we show that exciton diffusion is limited when the effective conjugation length of the polymer chain is decreased. Our findings further emphasize the importance of controlled syntheses accompanied by careful analyses.

In PCDTBT, both the cbz and TBT groups can form homocoupling bonds, but TBT homocoupling is negligible.³ We therefore refer to carbazole homocoupling (cbz-cbz) simply as homocoupling (hc) in the following. The hc concentration was determined experimentally by NMR spectroscopy (see Methods section and Supporting Information) and refers to the total number of homocoupling bonds in the chain divided by all bonds (alternating bonds + homocoupling bonds).

A variety of techniques for measuring exciton diffusion is applied in the literature.⁹,¹⁰ We used the bulk quenching method to determine the exciton diffusion coefficient and length at room temperature. This technique compares photoluminescence (PL) decay of films with different concentrations of embedded quencher molecules.¹¹ As quenchers, we used PC₆₁BM (phenyl-C₆₁-butyric acid methyl ester) assuming a quenching efficiency of unity and a quenching radius r ≈ 1 nm.¹¹,¹² In films of organic semiconductors, usually one recombination mechanism is dominant. We extracted the corresponding PL lifetime τ with PL(t) ∝ exp(−t/τ). Measuring τ as a function of the quencher concentration c yields the exciton diffusion coefficient D with the Stern–Volmer equation⁸,¹³,

\[ \frac{1}{\tau(c)} = \frac{1}{\tau_0} + 4 \pi r D c. \]  

(1)

The three-dimensional (Z = 3) diffusion length¹³ \( L_D \) results from the radiative lifetime \( \tau_0 \) of the pristine material and D (note that the factor 2 is sometimes omitted and that often the one-dimensional case is considered in the literature),

\[ L_D = \sqrt{2ZD\tau_0}. \]  

(2)
II. RESULTS

We first compare exciton diffusion in films between 0% and 10% hc samples with comparable number average molecular weight ($M_{n,SEC} = 27.6 \text{ kg/mol}$ and $31.0 \text{ kg/mol}$, respectively). Figure 1a) shows the PL decay of PCDTBT with 0% hc. The decay of a film with 0.4 wt% PCBM is shorter because excitons reach PCBM molecules and are quenched in accordance to equation (1). Figure 1b) shows the decay for 10% hc. Here, we observed an identical decay until $t = 4 \text{ ns}$. The initial decay of pristine film and blend yielded the same lifetime of $\tau = 699 \text{ ns}$. We found shorter lifetimes at 2 wt% of PCBM (see Stern–Volmer plot in the Supporting Information). The difference between Fig. 1a) and b) indicates a changed exciton diffusion. Fitting with the Stern–Volmer equation (1) yielded an exciton diffusion coefficient $D = 0.63 \cdot 10^{-4} \text{ cm}^2\text{s}^{-1}$ for 0% hc and $D = 0.06 \cdot 10^{-4} \text{ cm}^2\text{s}^{-1}$ for 10% hc. Ward et al. found $D = (1.1 \pm 0.5) \cdot 10^{-4} \text{ cm}^2\text{s}^{-1}$, in agreement with our results considering the error bars.\textsuperscript{14}

We additionally measured diffusion in a commercial PCDTBT batch with 2.5% hc, $M_{n,SEC} = 22.3 \text{ kg/mol}$ and a batch with 6% hc, $M_{n,SEC} = 45.8 \text{ kg/mol}$. The molecular weight of both batches deviated from the 0% hc batch by −20% and +50%, respectively. Nevertheless, our results for $D$ fitted the trend that the diffusion length decreases for higher homocoupling concentration, as shown in Fig. 2.

To assess the possible influence of the mentioned molecular weight deviations, we measured $D$ for three 0% hc and two 6% hc batches with varying molecular weight. Figure 3 shows that the lowest molecular weight resulted in the shortest diffusion length. At 0% hc, we found a maximum at 27.6 kg/mol. It is not clear if such maximum exists in the case of 6% hc. However, we observed that low molecular weights decrease $L_D$ with and without homocoupling in the polymer chain. With these findings, we can reevaluate Fig. 2. The $L_D$ of the 2.5% hc batch is underestimated because of the 20% lower $M_{n,SEC}$. In contrast, $L_D$ of the 6% hc batch overestimated because of the 50% higher $M_{n,SEC}$. In summary, we find evidence for monotonously decreasing exciton diffusion coefficient and length with increasing carbazole homocoupling concentration in PCDTBT at a given molecular weight.
III. DISCUSSION

We now discuss the interaction between excitons and homocouplings by evaluating quenching, traps and the distribution of homocoupling defect sites in the chain. The bulk quenching method compares PL lifetimes of a pristine and quenched film, as described above. We now hypothetically consider carbazole homocoupling defects as perfect quenchers with the same properties as PCBM molecules (quenching radius $r \approx 1$ nm, homogeneously distributed in the film). From the PCDTBT film density$^{15}$ of $\rho = 1.16 \text{g cm}^{-3}$ and $M_{n, \text{SEC}} = 31.0 \text{kg/mol}$ follows a homocoupling defect concentration of $c_{\text{hc}} \approx 10^{20} \text{cm}^{-3}$ in the 10 $\%$ hc film. We now compare the lifetime of both films. The 0 $\%$ hc film with $\tau_0 = 828 \text{ns}$ has a longer lifetime than the 10 $\%$ hc pristine film ($\tau_0 = 699 \text{ns}$). Equation (1) yields a hypothetical value of $D \approx 0.02 \cdot 10^{-4} \text{cm}^2 \text{s}^{-1}$ for the 0 $\%$ hc film which corresponds to only 3 $\%$ of our experimental value. We therefore conclude that the interaction between homocoupling defects and excitons cannot be described as quenching.

Several studies have shown that trap states decrease the diffusion length in organic semiconductor films.$^{16-18}$ PCDTBT films have low structural order and are amorphous.$^{19,20}$ Exciton diffusion is isotropic in PCDTBT.$^{14}$ We assume that exciton diffusion can be described as interchain hopping with only weak contribution of intrachain processes.$^{21-24}$ We now discuss if homocoupling defects act as exciton traps. Lombeck et al. found that carbazole homocoupling defects cause a localization of the LUMO on the neighboring TBT groups. The highest occupied molecular orbital (HOMO) energy thereby decreases by 0.02 eV and the LUMO by 0.05 eV.$^3$ If we assume homocoupling defect sites as randomly distributed trap sites in the film, we can relate the homocoupling concentration to the number of traps in the film, $hc \propto c_{\text{trap}}$. Anthanassopoulos et al.$^{13}$ simulated the influence of a trap concentration $c_{\text{trap}}$ on the diffusion length and found it to be in agreement with analytic predictions by Montroll$^{22}$ with $L_D \propto c_{\text{trap}}^{-1/3}$. Mikhnenko et al. found $L_D \propto c_{\text{trap}}^{-1/3}$ by comparing the calculated intrinsic $c_{\text{trap}}$ and its influence on diffusion for different materials.$^{16}$

All studies find a strong dependence of $L_D$ on traps, scaling with an inverse exponential law. However, our result (Fig. 2) shows only weak or no dependence in the regime between 0 – 2.5 $\%$ hc as discussed above. Thus, we believe that traps are (similar to quenchers) insufficient in describing the limitation of exciton diffusion caused by homocoupling. Another argument is the molecular weight dependence in the 6 $\%$ hc batches on $D$ and $L_D$. If homocoupling defects acted as traps for excitons, diffusion characteristics would be less dependent on molecular weight and strongly correlated with $c_{\text{trap}} \propto hc$ between 0 – 2.5 $\%$ hc.

The maximum available space for delocalization of the exciton is set by the effective conjugation length of the polymer.$^{26}$ Note that exciton delocalization length and effective conjugation length are not equal.$^{27}$ The conjugated subunit is called chromophore. The effective conjugation length of a polymer can be limited by local chain defects and distortions which act as conjugation break.$^{26,28}$ In a disordered film it is unlikely that the full length of a copolymer chain can provide space for an exciton to delocalize (we refer to this as free conjugation length in the following). Realistically, the average effective conjugation length in polymers consists of a few repeat units.$^{29}$ As reported by Lombeck et al., carbazole homocoupling defects lead to a localization of the LUMO. From this finding we assume that homocoupling sites can limit the conjugation length. We evaluated the relevance of such hypothetical conjugation breaks by simulating the sequences of cbz and TBT in straight polymer chains. We considered carbazole homocoupling as randomly distributed occurrences of (cbz-cbz-TBT) segments within alternating (cbz-TBT)$_n$ polymer chains with Gaussian distributed molecular weight. We then evaluated the uninterrupted free conjugation length distribution by counting strictly alternating (cbz-TBT) sequences along each chain, setting the counter to zero whenever homocoupling occurred. This estimation assumes ideal polymer chains without kinks and twists and therefore represents the upper limit of free conjugation length. Figure 4 shows three representative model distributions of free conjugation lengths along the polymer chain in a film with $M_n = (30 \pm 5) \text{kg/mol}$ and $hc = \{0,1,10\}$ $\%$. In case of 0 $\%$ hc, the free conjugation length follows the Gaussian distribution of the molecular weight. The 1 $\%$ hc estimation shows a broad distribution which also includes very short conjugation lengths below 10 repeat units of CDTBT. At 10 $\%$ hc, most chromophores are shorter than four CDTBT repeat units. These surprising changes in the distribution can easily be understood when considering that only 33 $\%$ hc already result in a non-alternating (cbz-cbz-TBT)$_n$ sequence. In this case, the conjugation length would exclusively be one CDTBT unit, according to our definition of alternating (cbz-TBT)$_n$ sequences building up the chromophore.

The hopping of excitons between localized sites can be described as energy downhill migration from higher to lower localized states.$^{26,30}$ The distribution of these localized states is influenced by the local energetic environment, trap states and variability of conjugation length.$^{31}$ In a previous work, we showed that even identical chromophores can have different absorption and emission energies due to the energetic disorder of the local environment in a polymer film.$^{32}$ However, we now assume similar spatial disorder, energetic disorder and trap states in the films and discuss only the influence of chromophore distribution. As shown in Fig. 4, 10 $\%$ hc lead to an exponential distribution of chromophores. Most polymer sequences in the 10 $\%$ hc film are (cbz-cbz-TBT-cbz). These segments contain only one CDTBT unit. Banej et al. showed that in PCDTBT, the HOMO increases by 0.15 eV and the LUMO decreases by 0.08 eV when the conjugation length is increased from one to four
The influence of conjugation length on exciton diffusion was studied by Hennebicq et al.\textsuperscript{24} They found increased site to site coupling between shorter chromophores. This may explain the decrease of $\tau_0$ in films with homocoupling and short chain lengths (see Supporting Information). However, such increased coupling mostly affects chromophores with similar length and energy. We believe that the one order of magnitude decrease of the diffusion coefficient results from downhill migration within the exponential distribution of chromophores. In the 10 % homocoupling film, excitons may only hop between a few sites until they reach a longer chromophore with lower energy. These low energy chromophores can act as a trap due to the large energy difference.\textsuperscript{26,31} In contrast, the 1 % homocoupling film has a broad distribution of maximum free conjugation length, mostly uninterrupted by homocoupling defects. Energy differences between these longer chromophores are smaller.\textsuperscript{29} We expect the resulting distribution of chromophores in films with medium and high molecular weight and low hc concentrations to be similar because spatial disorder of the chains is the main limitation of conjugation lengths.\textsuperscript{26} The model explains why $D$ was similar in the two different 0 % hc films (27.6 and 50.7 kg/mol) as well as in the 2.5 % hc film (22.3 kg/mol). Although 2.5 % hc is a significant concentration of defects, the average effective conjugation length is similar to films with 0 % hc. This finding is also in agreement with Lombeck et al. who did not find significant changes of short circuit current between 0–3.4 % hc at 30 kg/mol in PCDTBT:PC$_{71}$BM solar cells.\textsuperscript{3}

To summarize all values of the experiment and to comprehend the interplay of homocoupling and chain length, we used our model to provide a rough estimate of the average free conjugation length $\langle N_{\text{eff}} \rangle$ for each polymer batch. Figure 5 shows the sharp decline of $\tau_0$ and $D$ when $\langle N_{\text{eff}} \rangle < 10$ CDTBT repeat units. Considering exciton diffusion with respect to $\langle N_{\text{eff}} \rangle$ also explains the non-intuitive finding that $D$ is similar for a defect-free film with short chains (0 % hc, 6.2 kg/mol) and a high homocoupling film with long chains (6 % hc, 45.8 kg/mol). Both polymers share a similar value of $\langle N_{\text{eff}} \rangle \approx 9$ and 7, respectively. Photoluminescence measurements in solution confirmed the plausibility of an average free conjugation length (see Supporting Information). The three samples with the lowest values of $\langle N_{\text{eff}} \rangle$ showed a 30 meV shift of the main peak towards higher energies.
length according to our experimental polymer parameters ($h_c$, $M_{n,SEC}$). Exciton diffusion coefficient $D$ and intrinsic lifetime $\tau_0$ were significantly lower in batches with an average free conjugation length smaller than 10 CDTBT repeat units. These short average conjugation lengths occur in homocoupling defect-free films with low molecular weight below 10 kg/mol as well as in films with high homocoupling concentration. Finally, our results are consistent with observations from the literature regarding the connection between molecular structure and short circuit current of organic solar cells.$^2,3,33,34$

V. METHODS

The PCDTBT samples have been prepared as described in the Supporting Information. Carbazole homocouplings were intentionally introduced with varying amounts of an asymmetric carbazole monomer, similar to the synthesis procedure described previously.$^4$ Homocoupling concentration was determined by high-temperature NMR measurements. Molecular weights have been determined by high-temperature size exclusion chromatography in trichlorobenzene at 150 °C. Molecular weight, dispersity, homocoupling concentration and experimental values are given in the Supporting Information. Conventional PCDTBT with 2.5 \% \textit{hc} was purchased from Alfa Aesar. The authors declare no competing financial interest.

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Appendix B: Author contributions

M. Streiter built the experimental setup and measured exciton diffusion supported by F. Meier. M. Streiter interpreted the results and wrote the manuscript. D. Beer prepared the samples. C. Lienert and F. Lombeck synthesized PCDTBT of varying \textit{hc} content. M. Sommer supervised the synthetic work and was involved in discussions and writing the manuscript. C. Deibel supervised the experimental work and contributed to interpretation of results and writing of the manuscript.

Appendix C: Notes

The authors declare no competing financial interest.

Appendix D: Supplementary Information

Synthesis of PCDTBT, analysis of molecular weight and homocoupling, Stern–Volmer plots, PL spectra in solution.

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Supporting Information

Homocoupling defects limit exciton diffusion in a conjugated polymer

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TABLE I. List of measured PCDTBT batches with different molecular weight and carbazole homocoupling (hc) concentration.

| batch lab ID | $M_n,SEC$ [kg/mol] | hc [mol%] | $\tau_0$ [ns] | $D$ $[10^{-4}\text{cm}^2\text{s}^{-1}]$ |
|--------------|-------------------|-----------|--------------|-----------------|
| 1 CL10,CF    | 6.2               | 0         | 724          | 0.32            |
| 2 CL26,CF    | 9.4               | 6         | 644          | 0.15            |
| 3 FL498      | 31.0              | 10        | 699          | 0.06            |
| 4 CL24       | 27.6              | 0         | 828          | 0.63            |
| 5 CL12       | 50.7              | 0         | 862          | 0.50            |
| 6 Commercial | 22.3              | 2.5       | 850          | 0.51            |
| 7 CL27       | 45.8              | 6         | 672          | 0.37            |

INSTRUMENTS

High temperature size exclusion chromatography (HT-SEC)

HT-SEC was performed on an Agilent PL GPC 220 in 1,2,4 trichlorobenzene at 150°C and a flow rate of 1 ml/min. Two 2x Agilent Mixed-B-LS columns were used for separation. Polystyrene calibration was used. HT-SEC spectra are shown in figure (1).

NMR spectroscopy

$^1$H NMR spectroscopy (500.13 MHz) of polymers was performed with a Bruker Avance III spectrometer using a 5 mm BBI gradient probe at 120°C. C$_2$D$_2$Cl$_4$ ($\delta(^1\text{H}) = 5.98$ ppm) was used as solvent. NMR spectra are shown in figure (2).

Photoluminescence spectroscopy

Steady state photoluminescence spectra were measured in dichlorobenzene solution (polymer concentration 0.025 mg/ml) with a Varian Cary Eclipse spectrometer in quartz cuvettes. The excitation wavelength was 532 nm. Spectra of all batches are shown in figure (5).
SYNTHESIS OF PCDTBT

Batch 1

4,7-Bis(5-bromothiophen-2-yl)benzo[c][1,2,5]thiadiazole (TBT-Br$_2$) (627 mg, 1.37 mmol) and 9-(heptadecan-9-yl)-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (Cbz-Bpin$_2$) (900 mg, 1.37 mmol) were loaded in a 100 ml screw cap vial. Under argon atmosphere the catalyst Pd(PPh$_3$)$_4$ was added and the vial closed with a new septum. Toluene (27.4 ml) and an aqueous 2M K$_2$CO$_3$ solution (27.4 ml) were purged with nitrogen for 20 min. The solvent mixture and 3 drops Aliquat 336® were added to the reaction vial. The septum was displaced by a screw cap under a stream of nitrogen and the reaction mixture was heated at 80°C under vigorous stirring. After 112 h, the mixture was allowed to cool to room temperature. The aqueous layer was removed and 1,2-dichlorobenzene was added to the organic layer to dissolve solid components. The resulting polymer was precipitated into methanol, filtered and washed by Soxhlet extraction with methanol, acetone, hexanes, chloroform, and chlorobenzene. The chloroform fraction was collected, filtered over silica gel and concentrated under vacuum. The polymer was precipitated into methanol and dried under vacuum.

Yield (chloroform fraction): 87%
(SEC, TCB, 150°C) $M_n = 6.2$ kg/mol, $M_w/M_n = 5.32$, hc: 0 mol%

Batch 2

TBT-Br$_2$ (589 mg, 1.23 mmol), Cbz-Bpin$_2$ (846 mg, 1.23 mmol), and 2-bromo-9-(heptadecan-9-yl)-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (Bpin-Cbz-Br) (100 mg, 0.164 mmol) were loaded in a 100 ml screw cap vial. Under argon atmosphere the catalyst Pd(PPh$_3$)$_4$ was added and the vial closed with a new septum. Toluene (27.4 ml) and an aqueous 2M K$_2$CO$_3$ solution (27.4 ml) were purged with nitrogen for 20 min. The solvent mixture and 3 drops Aliquat 336® were added to the reaction vial. The septum was displaced by a screw cap under a stream of nitrogen and the reaction mixture was heated at 80°C under vigorous stirring. After 24 h, the mixture was allowed to cool to room temperature. The aqueous layer was removed and 1,2-dichlorobenzene was added to the organic layer to dissolve solid components. The resulting polymer was precipitated
into methanol, filtered and washed by Soxhlet extraction with methanol, acetone, hexanes, chloroform, and chlorobenzene. The chloroform fraction was collected, filtered over silica gel and concentrated under vacuum. The polymer was precipitated into methanol and dried under vacuum.

Yield (chloroform fraction): 89 %
(SEC, TCB, 150 °C) $M_n = 9.4 \text{ kg/mol}$, $M_w/M_n = 3.86$, hc: 6 mol%

**Batch 3**

TBT-Br$_2$ (300 mg, 0.65 mmol), Cbz-Bpin$_2$ (431 mg, 0.65 mmol), and BpinCbzBr (88.9 mg, 0.14 mmol) were loaded in a 100 ml screw cap vial. Under argon atmosphere the catalyst Pd(PPh$_3$)$_4$ was added and the vial closed with a new septum. Toluene (27.4 ml) and an aqueous 2M K$_2$CO$_3$ solution (27.4 ml) were purged with nitrogen for 20 min. The solvent mixture and 3 drops Aliquat 336® were added to the reaction vial. The septum was displaced by a screw cap under a stream of nitrogen and the reaction mixture was heated at 80 °C under vigorous stirring. After the reaction was completed, the mixture was allowed to cool to room temperature. The aqueous layer was removed and 1,2-dichlorobenzene was added to the organic layer to dissolve solid components. The resulting polymer was precipitated into methanol, filtered and washed by Soxhlet extraction with methanol, acetone, hexanes, chloroform, and chlorobenzene. The chlorobenzene fraction was collected and dried under vacuum.

Yield (chloroform fraction): 86 %
(SEC, TCB, 150 °C) $M_n = 31.0 \text{ kg/mol}$, $M_w/M_n = 2.90$, hc: 10 mol%

**Batch 4**

TBT-Br$_2$ (627 mg, 1.37 mmol) and Cbz-Bpin$_2$ (900 mg, 1.37 mmol) were loaded in a 100 ml screw cap vial. Under argon atmosphere the catalyst Pd(PPh$_3$)$_4$ was added and the vial closed with a new septum. Toluene (27.4 ml) and an aqueous 2M K$_2$CO$_3$ solution (27.4 ml) were purged with nitrogen for 20 min. The solvent mixture and 3 drops Aliquat 336® were added to the reaction vial. The rubber seal was replaced by a Teflon seal under a stream of nitrogen and the reaction mixture was heated at 80 °C under vigorous stirring. After
72 h the mixture was allowed to cool to room temperature. The aqueous layer was removed and the resulting polymer was precipitated into methanol, filtered and washed by Soxhlet extraction with methanol, acetone, hexanes, chloroform, and chlorobenzene. The polymer was precipitated into methanol, filtered and dried under vacuum.

**Yield (chloroform fraction): 57%**

(SEC, TCB, 150°C) $M_n = 27.6$ kg/mol, $M_w/M_n = 2.86$, hc: 0 mol%

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**Batch 5**

TBT-Br$_2$ (100 mg, 0.218 mmol), Cbz-Bpin$_2$ (143 mg, 0.218 mmol), the catalyst precursor Pd$_2$dba$_3$ (1.0 mg, 0.5 mol%), and the ligand PPh$_3$ (11.4 mg, 20 mol%) were loaded in an 18 ml screw cap vial. Toluene (8.7 ml) and an aqueous 2M K$_2$CO$_3$ solution (8.7 ml) were purged with nitrogen for 20 min. The solvent mixture and 1 drop Aliquat 336® were added to the reaction vial under nitrogen atmosphere. The septum was displaced by a screw cap under a stream of nitrogen and the reaction mixture was heated at 80°C under vigorous stirring. After 72 h, the mixture was allowed to cool to room temperature. The aqueous layer was removed. The resulting polymer in the organic layer was precipitated into methanol, filtered and washed by Soxhlet extraction with methanol, acetone, hexanes, chloroform, and chlorobenzene. The chlorobenzene fraction was poured into methanol to precipitate the polymer. The solvent was decanted and the polymer was dried under vacuum.

**Yield (chloroform fraction): 87%**

(SEC, TCB, 150°C) $M_n = 50.7$ kg/mol, $M_w/M_n = 2.25$, hc: 0 mol%

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**Batch 7**

TBT-Br$_2$ (589 mg, 1.23 mmol), Cbz-Bpin$_2$ (846 mg, 1.23 mmol), and BpinCbzBr (100 mg, 0.164 mmol) were loaded in a 100 ml screw cap vial. Under argon atmosphere the catalyst Pd(PPh$_3$)$_4$ was added and the vial closed with a new septum. Toluene (27.4 ml) and an aqueous 2M K$_2$CO$_3$ solution (27.4 ml) were purged with nitrogen for 20 min. The solvent mixture and 3 drops Aliquat 336® were added to the reaction vial. The septum was displaced by a screw cap under a stream of nitrogen and the reaction mixture was heated at 80°C under vigorous stirring. After the reaction was completed, the mixture was allowed
to cool to room temperature. The aqueous layer was removed and 1,2-dichlorobenzene was added to the organic layer to dissolve solid components. The resulting polymer was precipitated into methanol, filtered and washed by Soxhlet extraction with methanol, acetone, hexanes, chloroform, and chlorobenzene. The chlorobenzene fraction was precipitated into methanol, the mixture centrifuged and the solids dried under vacuum.

Yield (chloroform fraction): 53% 

(SEC, TCB, 150 °C) $M_n = 45.8$ kg/mol, $M_w/M_n = 2.58$, hc: 6 mol%

FIG. 1. HT-SEC of samples 1-7 in trichlorobenzene at 150 °C.
FIG. 2. 500 MHz $^1$H-NMR ($\text{C}_2\text{D}_2\text{Cl}_4$, 120°C) of samples 1-7 (from top to bottom) showing the aromatic region. The signal at $\approx$ 8.2 ppm arises from carbazole homocoupling and was used for hc content determination.
FIG. 3. Stern–Volmer plot of inverse PL lifetimes $\tau^{-1}$ over quencher concentration $c$ in batches of PCDTBT with low homocoupling concentrations.

FIG. 4. Stern–Volmer plot of inverse PL lifetimes $\tau^{-1}$ over quencher concentration $c$ in batches of PCDTBT with high homocoupling concentrations.
FIG. 5. Steady state photoluminescence of all PCDTBT batches in dichlorobenzene solution. All spectra are normalized. Here we show the region of interest around the main peak.