Supporting Information to

The PCPDTBT family: correlations between chemical structure, polymorphism, and device performance

G.L. Schulz¹, F.S.U. Fischer¹, D. Trefz¹, A. Melnyk²,³, A. Hamidi-Sakr⁴, M. Brinkmann⁴, D. Andrienko², S. Ludwigs¹

UV-vis Absorption

Figure S1. Temperature-dependent absorption spectra of C-PCPDTBT in THF (3 mg/mL), measured in the temperature range between 55°C (red) and −15°C (blue) with 10°C temperature steps shown in grey. Spectrum measured at RT shown as dashed line.
Figure S2. Linear polarized UV-vis absorption spectra of HT rubbed PCPDTBT samples: (a) F-PCPDTBT and (b) Si-PCPDTBT. The rubbing direction R is parallel \( \parallel \) and \( \perp \) to the polarization direction. Optical dichroic ratios \( DR = A_\parallel/A_\perp \) amount to 2.3 (at 760 nm) and 2.1 (at 765 nm) for F-PCPDTBT and Si-PCPDTBT, respectively.
Simulations

Figure S3. Energy profiles of the dihedral angles between the donor and acceptor units (B3LYP functional, 6-311g(d,p) basis set).

A. Transfer integral distributions in PCPDTBT derivatives

Figure S4. Distributions of transfer integrals in three PCPDTBT derivatives in a π-stacked morphology. Inset shows the means of the distributions.
Using $\pi$-stacked morphologies, simulated with MD, we evaluated couplings between nearest neighbours in snapshots. Resulting distributions of $\log(\langle |J|^2 \rangle / eV^2)$ are shown in Figure S4, and contain 1280 points for each system. The means of the distributions are plotted in the inset, and show that, on average, Si-PCPDTBT exhibits highest couplings, while C-PCPDTBT the smallest. This is a consequence of a particular packing in a $\pi$-stack due to backbone and side-chain interactions.

B. Effect of geometry on transfer integral calculations

Very often electronic couplings decay with the distance $r$ between the centers of mass of two molecules (in a co-facial geometry) as $-\exp(-\alpha r)$, where $\alpha$ is a prefactor. Due to the similarity of HOMO orbitals of the three PCPDTBT systems, the prefactor $\alpha$ is also similar. Hence, reducing the inter-chain spacing distance $d$ from 4.0 Å (as in calculations depicted in Figure 1) to 3.6 Å (as observed in the $\pi$-stack simulations of C-PCPDTBT), would result in the same increase of couplings for all three polymers. Note that for mobility simulations transfer integrals were evaluated in $\pi$-stacked morphologies (Figure S4).

C. Role of dimer geometry on couplings

For electronic coupling calculations, (Figure 1), $d = 0$ matches the equilibrium geometry of a dimer in the $\pi$-stack. Hence, only a small range, $0 < d < 6$ Å, is shown. In the absence of side-chains, however, Si-PCPDTBT may have higher couplings than C-/F-PCPDTBT chains at a shift $d < 12$ Å, where both donor and acceptor units of the backbone are exactly on top of each other. Since this situation is never realized in the $\pi$-stacked morphologies it is not shown in Figure 1.
Figure S5. Characteristics of amorphous C-PCPDTBT films. (a) UV-vis absorption spectrum and AFM (b) height as well as (c) phase images of rather amorphous C-PCPDTBT films processed from CHCl₃. Corresponding TEM – bright field and electron diffraction images are shown in d) and e), respectively.³,⁴
Figure S6. Characteristics of C-PCPDTBT films exhibiting π-stacked polymer chains. (a) UV-vis absorption spectrum and AFM (b) height as well as (c) phase images of C-PCPDTBT films spincoated from CB/DIO. The corresponding electron diffraction pattern is shown in (d).
Figure S7. Absorption behavior and morphology of C-PCPDTBT films containing the dimer polymorph prepared by either spincoating from CHCl₃ followed by CS₂ vapor annealing (red, a-f) or melt-crystallization on oriented PTFE substrates (green, a,g,h). (a) UV-vis absorption spectra of the films. (b – f) Morphology of CS₂ vapor annealed films: AFM (b) height as well as (c) phase images, (d) TEM bright field, (e) electron diffraction pattern and (f) GIWAXS pattern. (g + h) Melt-crystallized films on oriented PTFE substrates: TEM (g) bright field and (h) electron diffraction pattern identifying the characteristic dimer traits. Images are adapted from references 4, 5 and 6.
Figure S8. Absorption behavior and morphology of F-PCPDTBT films exhibiting π-stacked polymer chains. (a) UV-vis absorption spectrum and AFM (b) height as well as (c) phase images of F-PCPDTBT films spincoated from CB. The corresponding TEM bright field image and electron diffraction pattern are shown in (d) and (e), respectively.4,6
Figure S9. Absorption behavior and morphology of F-PCPDTBT films containing the dimer structure prepared by high-temperature rubbing at 240°C. (a) UV-vis absorption spectrum and AFM (b) height as well as (c) phase images. The corresponding TEM bright field image and electron diffraction pattern are shown in (d) and (e), respectively.4,6
Figure S10. Absorption and Morphology of Si-PCPDTBT films with π-stacked polymer chains which were prepared by high-temperature rubbing at 230°C (a – e) and subjected to additional annealing at 280°C (f – i). (a) UV-vis absorption spectrum and AFM (b + f) height as well as (c + g) phase images. The corresponding TEM bright field image and electron diffraction pattern are shown in (d + h) and (e + i), respectively.
Figure S11. Absorption behavior and morphology of Si-PCPDTBT films containing the cross-hatched structure. (a – f): Films prepared by spincoating from CB at 80°C. (a) UV-vis absorption spectrum and AFM (b) height as well as (c) phase images. The corresponding TEM (d) bright field image, (e) high-resolution image and (f) electron diffraction pattern. (g + h): Films obtained by dropcasting from CB. TEM (g) high resolution image and (h) electron diffraction pattern.
Charge Transport Measurements

Table S1. Some representative hole mobilities measured in OFETs in bottom-gate top-contact (BGTC) and bottom-gate bottom-contact (BGBC) configuration and polymer molecular weights reported in the literature for C-/F-/Si-PCPDTBT.

<table>
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<tr>
<th></th>
<th>Transistor geometry</th>
<th>Deposition solvent</th>
<th>$\mu_{\text{sat}}$ (cm$^2$/V s)</th>
<th>Mw (kg/mol)</th>
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C-PCPDTBT

Figure S12. Characteristic output and transfer curves of OFETs made from C-PCPDTBT spincoated from CHCl₃ (mainly amorphous, a), spincoated from CB/DIO (π-stacked, b) and after SVA with CS₂ (dimer structure, c). Curves are averaged over one channel length.
Figure S13. Characteristic output and transfer curves of OFETs made from F-PCPDTBT spincoated from CB (π-stacked, a), rubbed parallel to the channel length (dimer structure, b) and rubbed perpendicular to the channel length (dimer structure, c). Curves are averaged over one channel length.
Figure S14. Characteristic output and transfer curves of OFETs made from Si-PCPDTBT spincoated from CB at 80°C (mostly cross-hatched, a), HT-rubbed parallel to the channel length (τ-stacked, b), HT-rubbed perpendicular to the channel length (τ-stacked, c) and after HT-rubbing and thermal annealing at 280°C for one hour (τ-stacked, d). Curves are averaged over one channel length.
References


