

Supporting Information

Influence of the position of the side chain on crystallization and solar cell performance of DPP-based small molecules

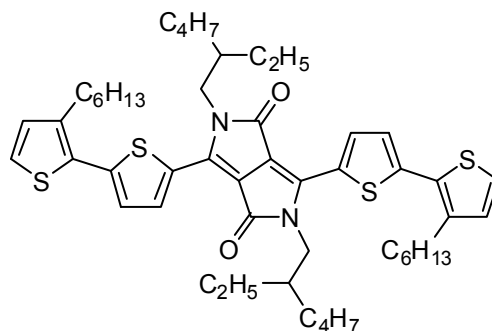
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1. Synthesis

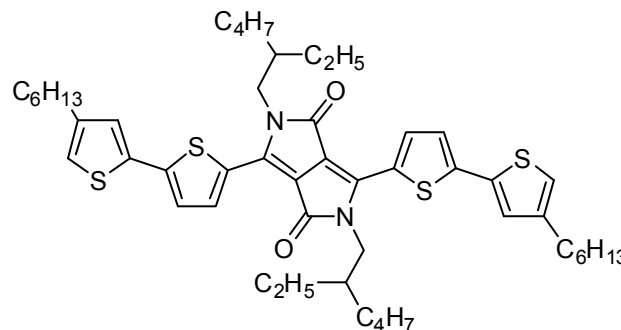
3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (1). 2,5-Bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (1.0 equiv., 2.2 g, 4.19 mmol)¹ was dissolved in dry chloroform (150 mL), covered from light with aluminum foil, and then *N*-bromosuccinimide (2.2 equiv., 1.64 g, 9.22 mmol) was added in one portion. After stirring at room temperature for 36 h, the reaction mixture was poured into cold (0 °C) water (200 mL) and extracted with chloroform (3 × 60 mL). The organic phase was washed with brine (2 × 100 mL), dried over MgSO₄, and the solvent was evaporated under reduced pressure. The dark-red residue was suspended in MeOH (30 mL), filtered, and the remaining crystals were washed with hot (60 °C) water (2 × 50 mL), cold MeOH (20 mL), and dried in vacuum. Yield: 2.5 g (87.4%). ¹H-NMR (400 MHz, CDCl₃): δ 8.67 (d, *J* = 4.2 Hz, 2H, Ar-*H*), 7.23 (d, *J* = 4.2 Hz, 2H, Ar-*H*), 3.97 (t, *J* = 8.0 Hz, 4H, -NCH₂-), 1.74-1.65 (m, 4H), 1.44-1.13 (m, 36H), 0.88-0.82 (m, 6H). ¹³C-NMR (400 MHz, CDCl₃): δ 160.99, 138.92, 135.09, 131.53, 131.20, 118.91, 107.98, 42.25, 31.81, 29.88, 29.52, 29.44, 29.38, 29.21, 29.09, 29.02, 26.75, 22.55, 13.90.

(1) Tamayo, A. B.; Tantiwivat, M.; Walker, B.; Nguyen, T.-Q., *J. Phys. Chem. C* **2008**, *112*, 15543-15552.

2,5-Bis(2-ethylhexyl)-3,6-bis(3'-hexyl-[2,2'-bithiophen]-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (DPP2T-3). To a solution of **(1)** (1 equiv., 0.6 g, 0.88 mmol) and 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Sigma-Aldrich, purity >95%) (3.0 equiv., 0.54 g, 2.60 mmol) in toluene (15 mL) under nitrogen atmosphere were added Aliquat®366 (3 drops) and aqueous Na₂CO₃ (2 M, 10 mL). The reaction mixture was degassed with an argon stream for 30 min. at room temperature, followed by addition of Pd[PPh₃]₄ (5 mol%, 50 mg, 0.04 mmol). The reaction mixture was stirred overnight at 115 °C, cooled back to the room temperature, precipitated into MeOH (200 mL), filtered, and washed with MeOH (50 mL) and cold acetone (10 mL). The crude product was purified by column chromatography on silica gel, using a mixture of 50:50 (v/v) dichloromethane/n-heptane, and subsequent precipitation from chloroform/methanol. Yield: 220 mg (70%). ¹H-NMR (400 MHz, CDCl₃): δ 9.02 (d, *J* = 4.1 Hz, 2H, Ar-*H*), 7.28 (d, *J* = 4.1 Hz, 2H, Ar-*H*), 7.26 (d, *J* = 5.2 Hz, 2H, Ar-*H*), 6.98 (d, *J* = 5.2 Hz, 2H, Ar-*H*) 4.06 (m, 4H, -NCH₂-), 2.83 (m, 4H, Th-CH₂-), 1.95 (m, 2H, -NCH₂CH(C₄H₉)(C₂H₅)), 1.67 (m, 4H, -N-CH₂CH₂-), 1.45 – 1.23 (m, 28H, -CH₂-), 0.94 – 0.84 (m, 18H, -CH₃). ¹³C-NMR (100 MHz, CDCl₃): δ 161.83, 142.24, 141.34, 139.84, 136.56, 130.69, 129.88, 129.00, 126.83, 125.36, 108.27, 46.21, 39.43, 31.85, 30.69, 29.80, 29.44, 28.57, 23.72, 23.28, 22.78, 14.20, 14.20, 10.67. MALDI-TOF-MS: *m/z* 856.50 (100%), 857.50 (70), 858.50 (41), 859.50 (21), 860.51 (10).



2,5-Bis(2-ethylhexyl)-3,6-bis(3'-hexyl-[2,2'-bithiophen]-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (DPP2T-4). The preparation of DPP2T-4 was carried out using the same procedure as for DPP2T-3 except using commercial 2-(3-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

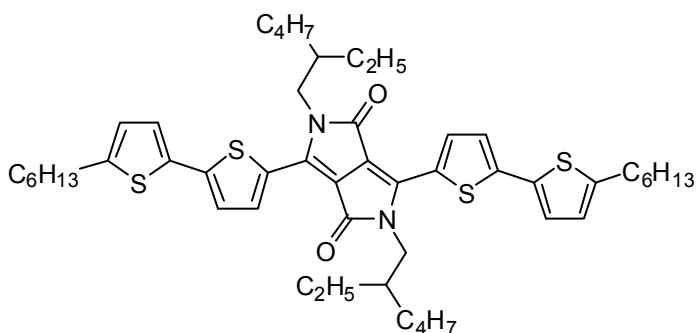


(Sigma-Aldrich, purity >95%). The crude product was purified by column chromatography on silica gel, using a mixture of 50:50 (v/v) dichloromethane/n-heptane, and subsequent

precipitation from chloroform/methanol. Yield: 220 mg (70%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 9.02 (d, $J = 4.1$ Hz, 2H, Ar-*H*), 7.28 (d, $J = 4.1$ Hz, 2H, Ar-*H*), 7.26 (d, $J = 5.2$ Hz, 2H, Ar-*H*), 6.98 (d, $J = 5.2$ Hz, 2H, Ar-*H*) 4.06 (m, 4H, - NCH_2 -), 2.83 (m, 4H, Th- CH_2 -), 1.95 (m, 2H, - $\text{NCH}_2\text{CH}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)$), 1.67 (m, 4H, - $\text{N-CH}_2\text{CH}_2$ -), 1.45 – 1.23 (m, 28H, - CH_2 -), 0.94 – 0.84 (m, 18H, - CH_3). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 161.83, 142.24, 141.34, 139.84, 136.56, 130.69, 129.88, 129.00, 126.83, 125.36, 108.27, 46.21, 39.43, 31.85, 30.69, 29.80, 29.44, 28.57, 23.72, 23.28, 22.78, 14.20, 14.20, 10.67. MALDI-TOF-MS: m/z 856.50 (100%), 857.50 (70), 858.50 (41), 859.50 (21), 860.51 (10).

2,5-Bis(2-ethylhexyl)-3,6-bis(5'-hexyl-2,2'-bithiophen-5-yl)pyrrolo[3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (DPP2T-5). The

preparation of DPP2T-5 was carried out using the same procedure as that for DPP2T-3 except that 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane² was used. The crude product was purified by



column chromatography on silica gel, using mixture of 50:50 (V:V) chloroform/n-heptane as the eluent. Yield: 0.55 g (92%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 8.92 (d, $J = 4.1$ Hz, 2H, Ar-*H*), 7.22 (d, $J = 4.1$ Hz, 2H, Ar-*H*), 7.12 (d, $J = 3.5$ Hz, 2H, Ar-*H*), 6.73 (d, $J = 3.5$ Hz, 2H, Ar-*H*), 3.98-4.08 (m, 4H, - NCH_2 -), 2.79-2.83 (m, 4H, Th- CH_2 -), 1.82-1.92 (m, 2H, - $\text{NCH}_2\text{CH}(\text{C}_4\text{H}_9)(\text{C}_2\text{H}_5)$), 1.65-1.73 (m, 4H, - $\text{N-CH}_2\text{CH}_2$ -), 1.27-1.40 (m, 28H, - CH_2 -), 0.82-0.92 (m, 18H, - CH_3). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3): δ 161.54, 147.67, 143.26, 139.30, 136.75, 133.63, 127.46, 125.29, 124.87, 123.94, 108.05, 45.92, 39.24, 31.53, 31.49, 30.34, 30.28, 28.74, 28.54, 23.67, 23.12, 22.55, 14.23, 14.07, 10.57. MALDI-TOF-MS: m/z 856.36 (100%), 858.37 (42), 860.35 (10).

(2) Barlow, S.; Odom, S. A.; Lancaster, K.; Getmanenko, Y. A.; Mason, R.; Coropceanu, V.; Brédas, J.-L.; Marder, S. R. *J. Phys. Chem. B* **2010**, *114*, 14397-14407.

2. Additional Figures

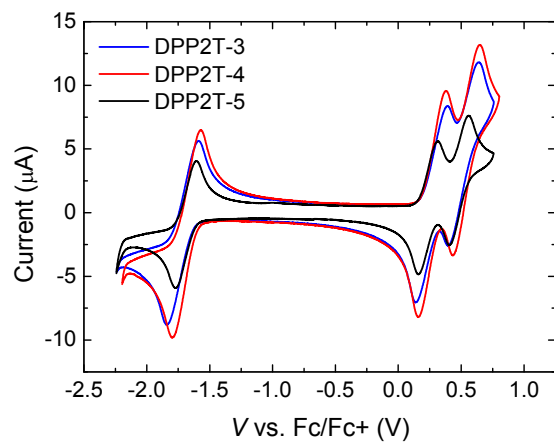


Figure S1. Cyclic voltammetry measurements of DPP2T-3, DPP2T-4 and DPP2T-5 molecules in *ortho*-dichlorobenzene electrolyte.

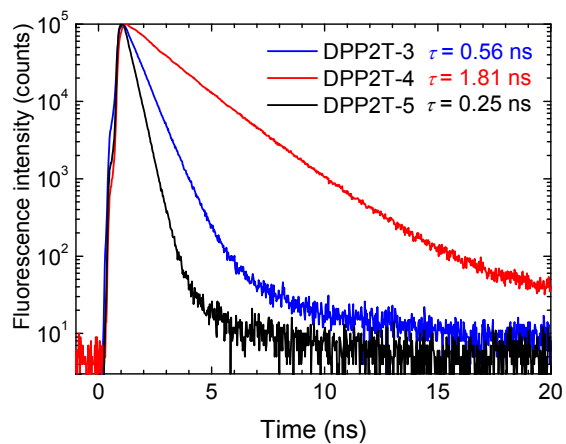


Figure S2. Time-resolved fluorescence at 725 nm of thin films of DPP2T-3, DPP2T-4, and DPP2T-5.

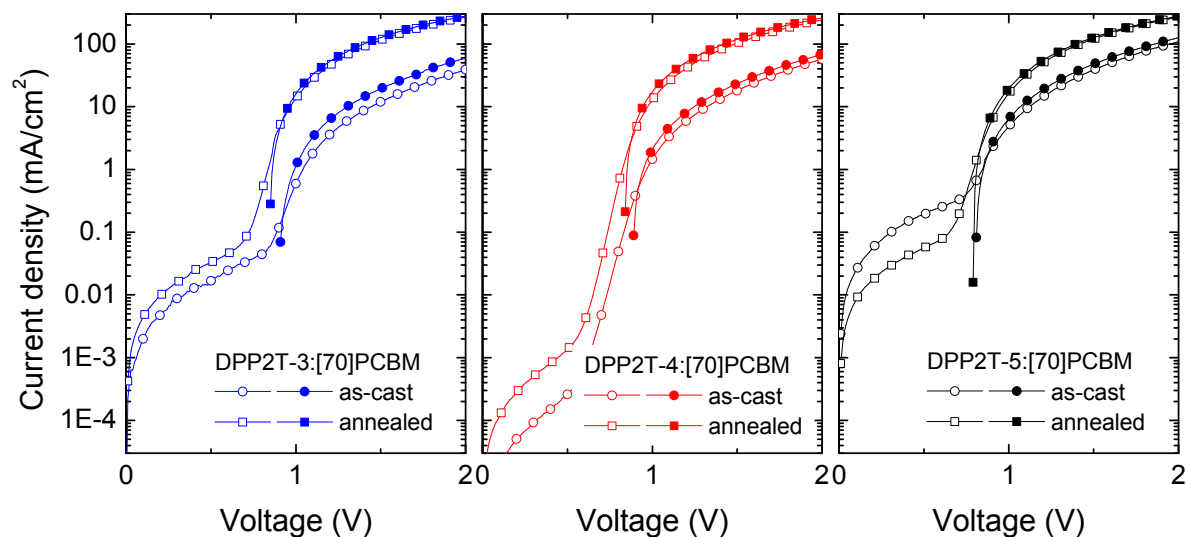


Figure S3. Semi-logarithmic plot of the J - V curves under forward bias of the optimized solar cells of DPP2T-3, DPP2T-4, and DPP2T-5 blended with [70]PCBM in a 2:1 weight ratio, as-cast and after 1 min. annealing at 100 °C (open symbols in dark and closed symbols under illumination). This graph represents the same data as shown in Figure 4 of the main text.

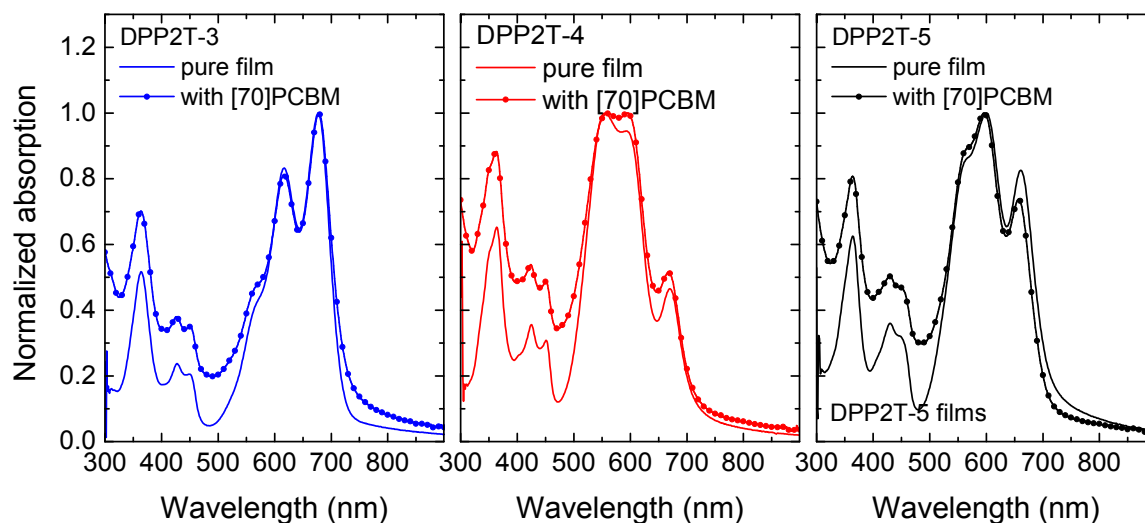


Figure S4. Normalized absorption spectra of pure DPP2T and DPP2T:[70]PCBM blend films in a 2:1 weight ratio after 1 min. annealing at 100 °C.

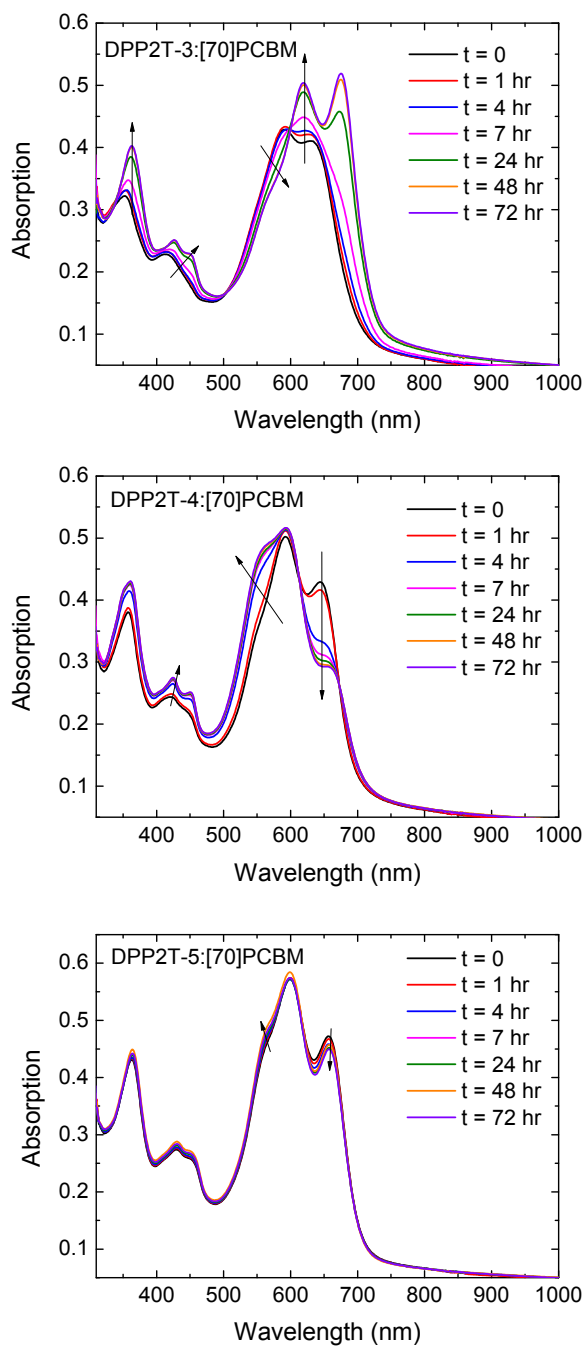


Figure S5. Evolution of optical absorption spectra of DPP2T:[70]PCBM blends over time at room temperature.

3. Simulation of GIWAXS diffraction patterns

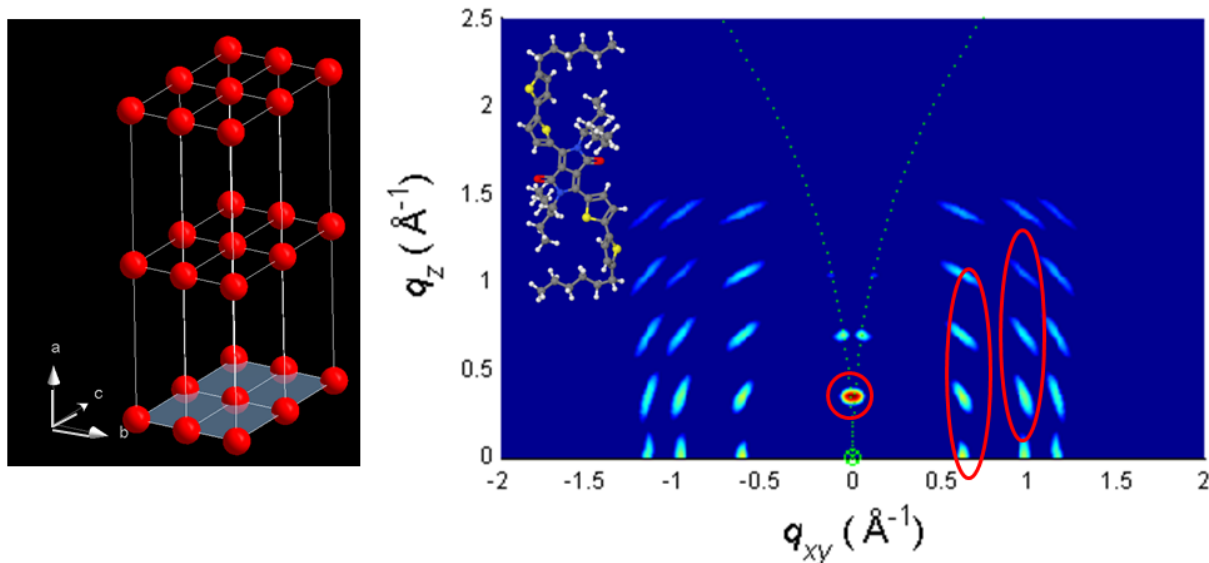


Figure S6. Left: space group used for simulations. Right: scattering pattern obtained from simulations for DPP2T-5; inset: possible arrangement of DPP2T-5 suitable for the obtained unit cell.

Using the software simDiffraction by Breiby^{S1} it is possible to reproduce the main features of the DPP2T-5 GIWAXS scattering pattern (marked in red). The basis of the calculations is the simple P1 space group with a rectangular unit cell and dimensions $a = 1.8$ nm, $b = 0.64$ nm, and $c = 1.0$ nm with an orientation as shown on the left. The inset of the simulated scattering pattern shows a possible shape of the DPP2T-5 molecule which would fit in such a unit cell and which is used to obtain the shown pattern. However, another shape could also be possible as long as the repeat units a , b , c remain unchanged. The molecules were built using Jmol^{S2} and altering (deleting and adding new atoms and bonds) previously published similar molecules as a starting point.^{S3} In Jmol typical bond lengths are taken into account and the final arrangement can be energetically minimized. It must be pointed out that while the positions of the molecules are well determined by the GIWAXS data it is not possible to determine the exact shape of the molecules without single crystal diffraction data. For example it is also not possible to distinguish whether b or c is parallel to the π -stacking direction of the backbone due to the isotropic distribution of both

parameters in the plane of the substrate. Body or face centred space groups can be excluded due to their significant deviation from the measured scattering pattern.

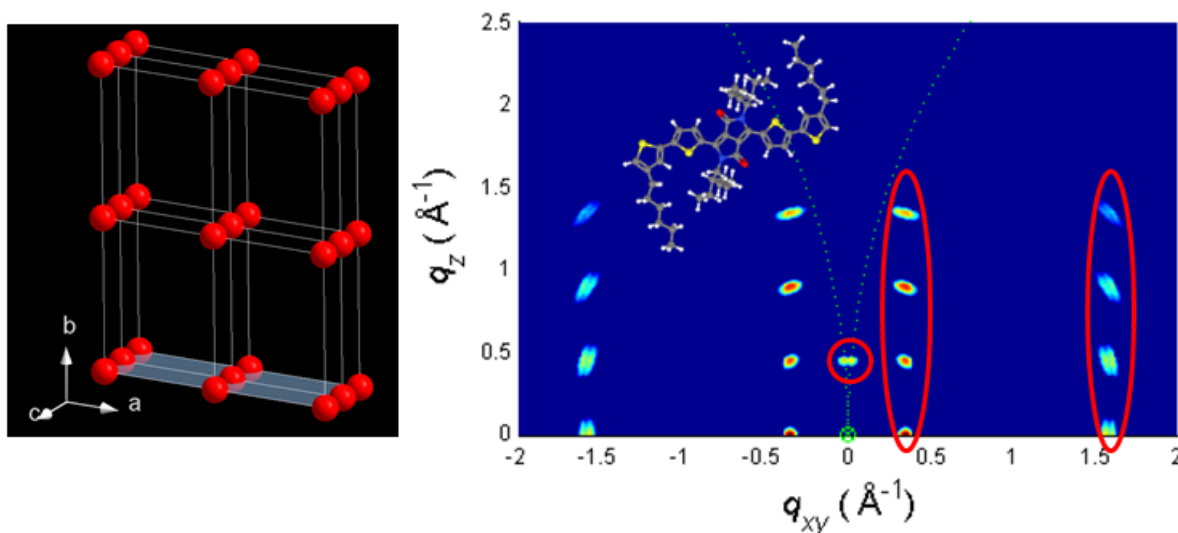


Figure S7. Left: space group used for simulations. Right: scattering pattern obtained from simulations for DPP2T-4; inset: possible arrangement of DPP2T-4 suitable for the obtained unit cell.

For DPP2T-4 also a rectangular unit cell with P1 space group symmetry decorated with the DPP2T-4 molecule is used to simulate the dominant pattern of the GIWAXS data. For unit cell dimensions of $a = 18$ nm, $b = 14$ nm, and $c = 4$ nm the experimental data is well reproduced. With the DPP2T-4 backbone parallel to the substrate as shown in the inset, the molecule can be efficiently packed into the unit cell. The same limitations apply as for Figure S6.

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- S1 Breiby, D. W.; Bunk, O.; Andreasen, J. W.; Lemke, H. T.; Nielsen, M. M. *J. Appl. Cryst.* **2008**, *41*, 262-271.
- S2 Jmol: an open-source Java viewer for chemical structures in 3D. <http://www.jmol.org/>
- S3 Qiao, Y.; Guo, Y.; Yu, C.; Zhang, F.; Xu, W.; Liu, Y.; Zhu, D. *J. Am. Chem. Soc.* **2012**, *134*, 4084–4087.