

Electronic Supplementary Information

The influence of siloxane side-chains on the photovoltaic performance of a conjugated polymer

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Materials and methods

All synthetic procedures were performed under a protective argon atmosphere. Commercial (dry) solvents and reactants were used without further purification, unless stated otherwise. *N*-bromosuccinimide (NBS) was recrystallized from deionized water prior to use. 1,4-Benzenediboronic acid bis(pinacol) ester and triphenylphosphine (PPh₃) were recrystallized from methanol prior to polymerization. Tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃) was purchased from Strem Chemicals Inc, [70]PCBM (purity 90-95%) was purchased from Solenne BV. All other chemicals and solvents were obtained from Sigma-Aldrich Co. 3,6-Di(thiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione and 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione were synthesized according to previously published procedures.^{S1} 1,5-Di-*tert*-butyl-1,1,3,5,5-pentamethyltrisiloxane was synthesized using a modified published procedure.^{S2}

¹H-NMR and ¹³C-NMR spectra were recorded on a Varian Mercury (¹H 400 MHz, ¹³C 100 MHz) spectrometer. Chemical shifts are given in ppm with respect to tetramethylsilane as internal standard. Matrix assisted laser desorption ionization time of flight (MALDI-TOF) mass spectrometry was measured on a Bruker Autoflex Speed spectrometer. GC-MS was measured on a system consisting of a Shimadzu (GC-2010) gas chromatograph and a Shimadzu (GCMS-QP2010plus) mass spectrometer. The gas chromatograph contained a 30 meter Phenomenex Zebron ZB-5MS column with an internal diameter of 0.25 mm and 0.25 μm stationary phase film thickness. The temperature programme consisted of a steady ramp from 80 °C to 300 °C over 8 minutes. Polymer molecular-weight distributions were estimated by GPC at 140 °C on a PL-GPC 120 system using a PL-GEL 10 mm MIXED-C column with *o*-DCB as the eluent and using polystyrene internal standards. Samples were dissolved at a concentration of 0.1 mg/ml in *o*-DCB at 140 °C for 1 h before being measured.

UV-vis-NIR absorption spectroscopy was conducted on a PerkinElmer Lambda 1050 spectrophotometer with a 3D WB PMT/InGaAs/PbS detector module. Solid films were obtained by spin coating (2000 rpm) solutions of the materials (6 mg/ml) in chloroform onto glass substrates which were

pre-cleaned with acetone and isopropanol, before being treated with UV-ozone for 30 minutes. Temperature-dependent spectra were recorded in TCE at temperatures between 20 °C and 100 °C using a PerkinElmer PTP1 Peltier temperature controller. Photoluminescence spectra were recorded with an Edinburgh Instruments FLSP920 double-monochromator luminescence spectrometer equipped with a nitrogen-cooled near-IR sensitive photomultiplier (Hamamatsu) using an excitation wavelength of 750 nm. Spectra were recorded of films processed onto glass substrates in a similar way to the samples used for the UV-vis-NIR spectroscopy measurements.

Square wave voltammetry was measured on the polymers in solid state which were deposited onto platinum wire by dipping the wire in the hot solutions (chloroform). A silver rod was employed as counter electrode and a silver chloride coated silver rod (Ag/AgCl) was used as a quasi-reference electrode. 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was used as electrolyte solution. The measurement was carried out under inert atmosphere with an AutoLab PGSTAT 12 at a scan speed of 0.125 V s⁻¹, a modulation amplitude of 20 mV and at a frequency of 25 Hz. Fc/Fc⁺ was employed as a standard with $E = -4.8$ eV.

The grazing incidence wide angle x-ray scattering (GIWAXS) experiments were carried out on a GANESHA 300 XL+ system from JJ X-ray equipped with a Pilatus 300K detector (pixel size 172 μm × 172 μm). The X-ray source was a Genix 3D Microfocus sealed tube X-ray Cu-source with integrated monochromator and the wavelength used was $\lambda = 1.5408$ Å. Transmission electron microscopy (TEM) was performed on a Tecnai G2 Sphera transmission electron microscope (FEI) operating at 200 kV.

Bottom-gate top-contact transistors were fabricated to investigate charge carrier transport for all polymers. The 300 nm thick SiO₂ dielectric was functionalized with octyltrichlorosilane (OTS) to minimize interfacial trapping sites. The polymer films were prepared by drop casting from 1 mg/ml chloroform solution in ambient atmosphere, following by annealing at 100 °C for 30 min in nitrogen atmosphere.

Photovoltaic devices with an active area of 0.09 and 0.16 cm² were fabricated in air on patterned indium tin oxide (ITO) glass substrates (Naranjo Substrates). The substrates were cleaned by sonication in acetone for 15 min., followed by scrubbing with a sodium dodecyl sulfate solution (99%, Acros), rinsing with deionized water, and a final sonication step in 2-propanol. Before deposition of the device layers the substrates underwent a 30 min. UV-ozone treatment. To obtain a ZnO layer, 0.5 M zinc acetate and 0.5 M ethanolamine were dissolved in 2-methoxyethanol by stirring overnight. The solution was then deposited onto the substrates by spin coating at 4000 rpm and annealing at 150 °C for 5 minutes. The substrates were then transferred to a nitrogen-filled glovebox to deposit the active layers. The active layers were deposited from a solution of polymer (5 mg/ml) and [70]PCBM (10 mg/ml) in chloroform containing 2%

of diphenyl ether. The solutions were heated to 90 °C for one hour to ensure that the polymers were completely dissolved, then kept at 60 °C and were finally cooled to room temperature under vigorous stirring during 2 minutes before spin coating at 2000 rpm. 10 nm of MoO₃ and 100 nm of Ag were deposited by thermal evaporation under high vacuum ($\sim 3 \times 10^{-7}$ mbar) as a back contact.

Current density – voltage (*J*–*V*) characteristics were measured with a Keithley 2400 source meter under ~ 100 mW/cm² white light illumination from a tungsten-halogen lamp filtered by a Schott GG385 UV filter and a Hoya LB120 daylight filter. The short-circuit current density (*J*_{sc}) was more correctly determined from external quantum efficiency (EQE) measurements by integration of the EQE with the AM 1.5G solar spectrum. EQE measurements were carried out under 1 sun operating conditions in a setup consisting of a modulated monochromatic light, a preamplifier (Stanford Research Systems SR570) and a lock-in amplifier (Stanford Research Systems SR830). The modulated monochromatic light was generated by using an optical chopper from Stanford Research Systems (SR540), an Oriel Cornerstone 130 monochromator and a 50 W (Osram 64610) tungsten-halogen lamp. The 1 sun conditions were provided by the use of a 730 nm LED (Thorlabs) at different intensities for appropriate bias illumination. The device was kept in a nitrogen-filled box with a quartz window. A calibrated silicon cell was used as reference prior to the *J*–*V* and EQE measurements.

Active layer thicknesses were determined with a Veeco Dektak150 profilometer.

Synthesis

2,5-Di(hex-5-ene)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (1**)**^{S3,S4}

3,6-Di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione^{S1} (2 g, 6.66 mmol) and potassium carbonate (2.76 g, 19.98 mmol) were dissolved in dimethylformamide (30 ml) and heated to 120 °C. Then 6-bromohexene (2.715 g, 16.65 mmol) was added and the mixture was kept at 120 °C for 3 h. The mixture was then allowed to cool down and kept refrigerated overnight to allow the product to crystallize. The solids were then filtered and washed multiple times with water and subsequently methanol. Compound **1** was obtained as dark purple solid with a yield of 2 g (65%) and used without further purification. ¹H NMR (400 MHz, CDCl₃) δ 8.92 (d, *J* = 3.1 Hz, 2H), 7.64 (d, *J* = 4.4 Hz, 2H), 7.29 (dd, 2H), 5.79 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 2H), 5.03 – 4.93 (m, 4H), 4.09 (t, *J* = 7.8 Hz, 4H), 2.11 (td, *J* = 7.4, 7.1 Hz, 4H), 1.77 (m, 4H), 1.52 (m, 4H). ¹³C NMR (400 MHz, CDCl₃) δ 161.36, 139.99, 138.29, 135.28, 130.70, 129.72, 128.64, 114.90, 107.70, 42.04, 33.35, 29.48, 26.15. MALDI-TOF-MS: [M⁺] calc: 464.16, found: 464.18.

1,5-Di-tert-butyl-1,1,3,5,5-pentamethyltrisiloxane (2)^{S2}

Tert-butyldimethylsilyl chloride (10 g, 66.35 mmol) and dichloromethylsilane (4.6 g, 40 mmol) were dissolved in isopropyl ether (15 ml) and added dropwise to a mixture of water (15 ml) and isopropyl ether (25 ml). After the dropwise addition, the whole mixture was heated to 70 °C for 24 h. The reaction mixture was then washed twice with water, once with saturated sodium bicarbonate and once with brine, before it was dried over MgSO₄ and the solvents were evaporated under reduced pressure. Three vacuum distillations (heating to 135 °C at 35 mbar) were then used to separate and purify the products, resulting the isolation of **2** in a purity of 96% and yield of 1.15 g (9.4%). ¹H NMR (400 MHz, CDCl₃) δ 4.67 (q, *J* = 1.6 Hz, 1H), 0.88 (s, 18H), 0.11 (d, *J* = 1.6 Hz, 3H), 0.05 (s, 12H). ¹³C NMR (400 MHz, CDCl₃) δ 25.62, 18.07, 1.61, -3.12. GC-MS: 4.00 min., *m/z*: 254, 211 and 135.

2,5-Bis(6-(1,5-di-tert-butyl-1,1,3,5,5-pentamethyltrisiloxan-3-yl)hexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (3)

2,5-Bis(hex-5-ene)-3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (**1**) (500 mg, 1.076 mmol) was dissolved in dry toluene (10 ml), degassed and kept under argon. 1,5-Di-tert-butyl-1,1,3,5,5-pentamethyltrisiloxane (**2**) (825 mg, 2.69 mmol) was then added and degassed, before 1 drop of Karstedt's catalyst was added. The mixture was kept under argon and heated to 80 °C overnight. The solvent was subsequently evaporated under reduced pressure and the solids were purified using column chromatography (2:8 dichloromethane:heptane, gradient to 4:6). Compound **3** was obtained in a yield of 60%. ¹H NMR (400 MHz, CDCl₃) δ 8.93 (dd, *J* = 3.9, 1.1 Hz, 2H), 7.63 (dd, *J* = 5.0, 1.1 Hz, 2H), 7.29 (dd, *J* = 5.0, 3.9 Hz, 2H), 4.07 (t, *J* = 7.9 Hz, 4H), 1.74 (m, 4H), 1.41 – 1.26 (m, 12H), 0.86 (s, 36H), 0.46 (t, *J* = 7.8 Hz, 4H), -0.02 (s, 24H), -0.00 (s, 6H). ¹³C NMR (400 MHz, CDCl₃) δ 161.55, 140.19, 135.44, 130.81, 129.97, 128.78, 107.88, 42.42, 33.14, 30.17, 26.84, 25.88, 23.32, 18.25, 17.86, 0.18, -2.74. MALDI-TOF-MS: [*M*+]
calc: 1076.53, found: 1076.55.

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(6-(1,5-di-tert-butyl-1,1,3,5,5-pentamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (4)

2,5-Bis(6-(1,5-di-tert-butyl-1,1,3,5,5-pentamethyltrisiloxan-3-yl)hexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**3**) (394 mg, 0.365 mmol) was dissolved in chloroform (6 ml), degassed with argon and cooled to 0° C. *N*-bromosuccinimide (135 mg, 0.768 mmol, 2.1 eq) was added and the mixture was kept at 0° C for 10 minutes before allowing to heat to room temperature. After 5.5 h the reaction mixture was extracted three times with water and the solvent was evaporated under

reduced pressure. The solids were then subjected to column chromatography (6:4 heptane:chloroform), then the purified product was dissolved in dichloromethane and precipitated in methanol before being dried. Compound **4** was obtained as a dark purple solid in a yield of 334 mg (74%). ^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, $J = 4.2$ Hz, 2H), 7.23 (d, $J = 4.2$ Hz, 2H), 3.98 (t, $J = 7.9$ Hz, 4H), 1.69 (m, 4H), 1.44 – 1.28 (m, 12H), 0.85 (s, 36H), 0.46 (t, $J = 7.7$ Hz, 4H), 0.02 (s, 24H), 0.00 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.00, 138.95, 135.31, 131.61, 131.09, 119.10, 107.79, 42.27, 32.89, 30.01, 26.60, 25.67, 23.08, 18.04, 17.64, -0.19, -2.94. MALDI-TOF-MS: $[\text{M}^+]$ calc: 1232.35, found: 1232.38.

General polymerization procedure

3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(6-(1,5-di-tert-butyl-1,1,3,5,5-pentamethyltrisiloxan-3-yl)hexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**4**), 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**5**) (together 1 eq), freshly recrystallized 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (**6**) (1 eq), recrystallized triphenylphosphine (1.5%), and $\text{Pd}_2(\text{dba})_3$ (6%) were loaded in a Schlenk tube and placed under argon. Toluene (2 ml) was added before degassing the solution with argon for 10 minutes. A 2 M solution of K_3PO_4 in water (5 eq) was then added together with one drop of Aliquad 336. The tube was subsequently sealed and heated to 115 °C and the mixture was left to react overnight. 1,1,2,2-Tetrachloroethane (TCE) (5 ml) was then added to dissolve the gel-like substance and this solution was precipitated in methanol. The solids were filtered, dissolved in TCE at 120 °C and stirred with ethylenediaminetetraacetic acid (200 mg) for 1 h before water was added and stirred for a further 1 h. The mixture was then cooled and extracted three times with water. The organic phase was reduced in volume under lowered pressure and then precipitated in methanol. Soxhlet extraction was then carried out on the solids with acetone, hexane, dichloromethane and chloroform. The solids left in the thimble were then dissolved in TCE at high temperature, after which the solvent was partially evaporated under reduced pressure and the polymer was precipitated in acetone. The solids were then filtered and dried.

100-PDPPTPT

4 (70 mg (56.7 μmol), **6** (18.9 mg, 56.7 μmol), $\text{Pd}_2(\text{dba})_3$ (1.56 mg, 1.7 μmol), triphenylphosphine (1.78 mg (6.8 μmol) and K_3PO_4 solution (0.14 ml) were used. GPC (o-DCB, 140 °C): $M_n = 10.9$ kDa, $M_w = 73.7$ kDa, $\mathcal{D} = 6.7$. Note: due to aggregation and tailing these numbers are approximate.

50-PDPPTPT

4 (54.5 mg, 44.1 μmol), **5** (40 mg, 44.1 μmol), **6** (29.1 mg, 88.2 μmol), $\text{Pd}_2(\text{dba})_3$ (1.21 mg, 1.32 μmol), triphenylphosphine (1.39 mg, 5.3 μmol) and of K_3PO_4 solution (0.22 ml) were used. GPC (o-DCB, 140 °C): $M_n = 2.7$ kDa, $M_w = 49.8$ kDa, $\mathcal{D} = 18.4$ Note: due to aggregation and tailing these numbers are approximate.

20-PDPPTPT

4 (21.0 mg, 17.0 μmol), **5** (61.6 mg, 67.9 μmol), **6** (28.0 mg, 84.8 μmol), $\text{Pd}_2(\text{dba})_3$ (1.16 mg, 1.27 μmol), triphenylphosphine (1.34 mg, 5.09 μmol), and K_3PO_4 solution (0.22 ml) were used. GPC (o-DCB, 140 °C): $M_n = 4.5$ kDa, $M_w = 45.5$ kDa, $\mathcal{D} = 10.0$. Note: due to aggregation and tailing these numbers are approximate.

10-PDPPTPT

4 (10.5 mg, 8.5 μmol), **5** (69.3 mg, 76.4 μmol), **6** (28.0 mg, 84.8 μmol), $\text{Pd}_2(\text{dba})_3$ (1.16 mg, 1.27 μmol), triphenylphosphine (1.34 mg, 5.09 μmol) and K_3PO_4 solution (0.22 ml) were used. GPC (o-DCB, 140 °C): $M_n = 15.6$ kDa, $M_w = 52.9$ kDa, $\mathcal{D} = 3.4$. Note: due to aggregation and tailing these numbers are approximate.

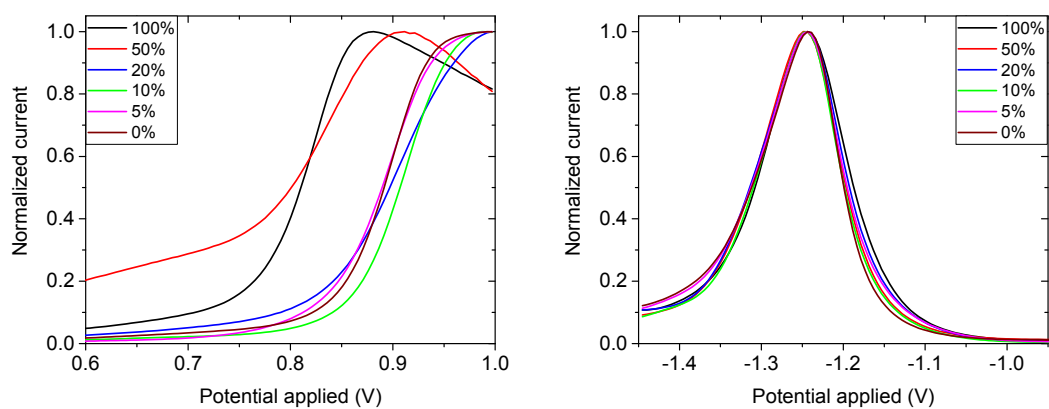
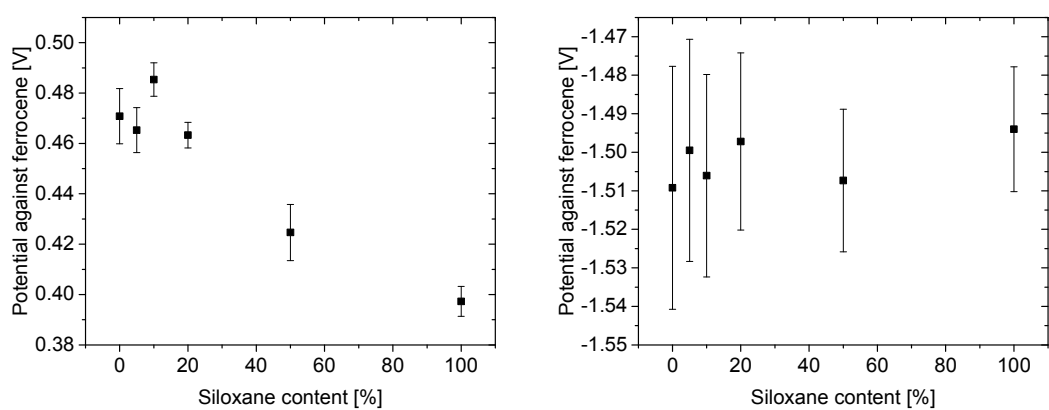
5-PDPPTPT

4 (4.24 mg, 5.24 μmol), **5** (73.1 mg, 80.6 μmol), **6** (28.0 mg, 84.8 μmol), $\text{Pd}_2(\text{dba})_3$ (1.16 mg, 1.27 μmol), triphenylphosphine (1.34 mg, 5.09 μmol) and K_3PO_4 solution (0.22 ml) were used. GPC (o-DCB, 140 °C): $M_n = 11.5$ kDa, $M_w = 56.0$ kDa, $\mathcal{D} = 4.9$. Note: due to aggregation and tailing these numbers are approximate.

0-PDPPTPT

5 (76.9 mg, 84.8 μmol), **6** (28.0 mg, 84.8 μmol), $\text{Pd}_2(\text{dba})_3$ (1.16 mg, 1.27 μmol), triphenylphosphine (1.34 mg, 5.09 μmol) and K_3PO_4 solution (0.22 ml) were used. GPC (o-DCB, 140 °C): $M_n = 21.2$ kDa, $M_w = 68.9$ kDa, $\mathcal{D} = 3.3$.

Supplementary figures

**Fig. S1.** Square wave voltammograms (oxidations and reductions) of the polymers.**Fig. S2.** Summary of the HOMO and LUMO energy levels measured by square wave voltammetry.

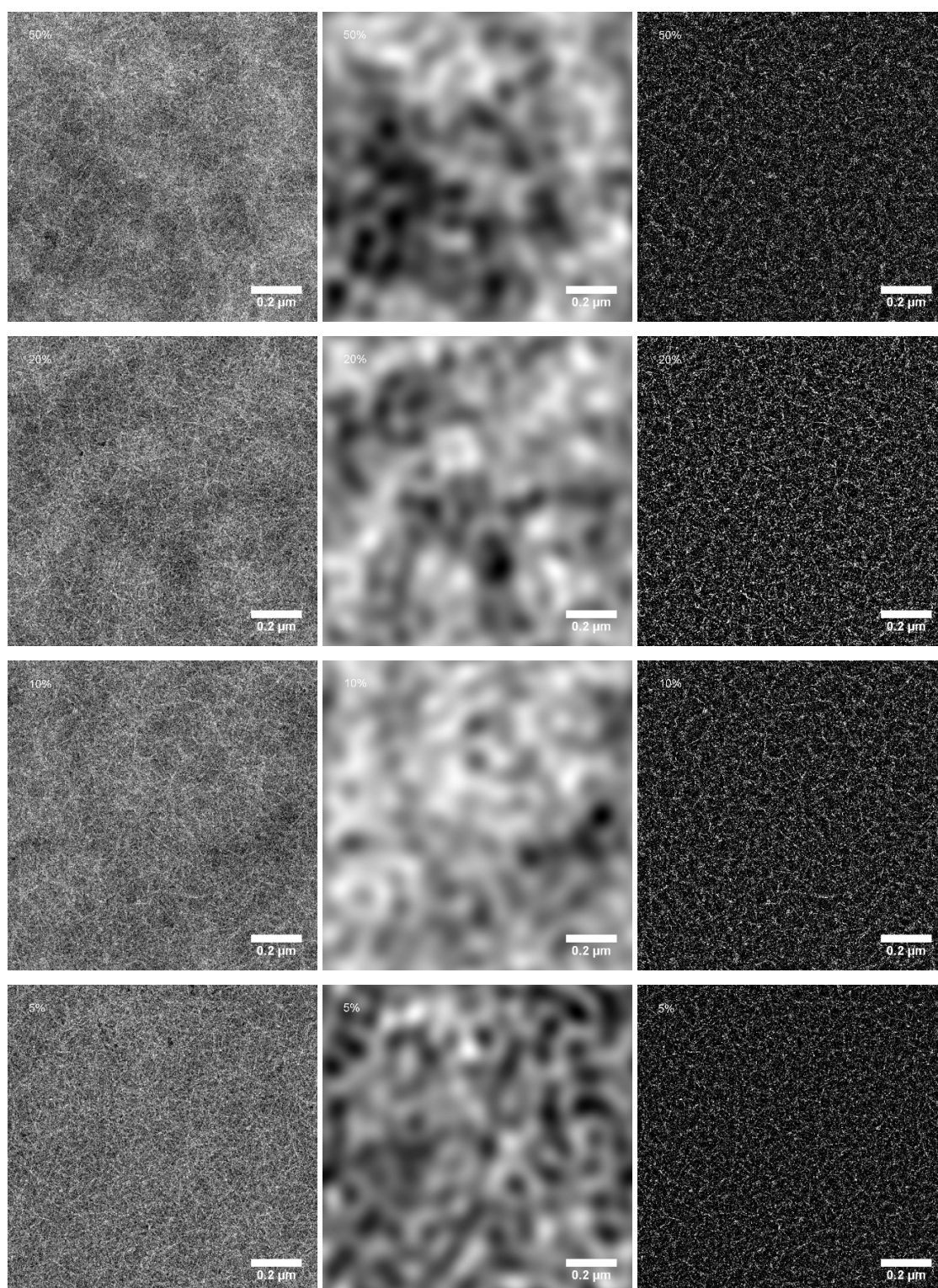


Fig. S3. Unfiltered (left) and Fourier filtered (right) TEM images of the 50%, 20% 10% and 5% siloxane polymers (top to bottom).

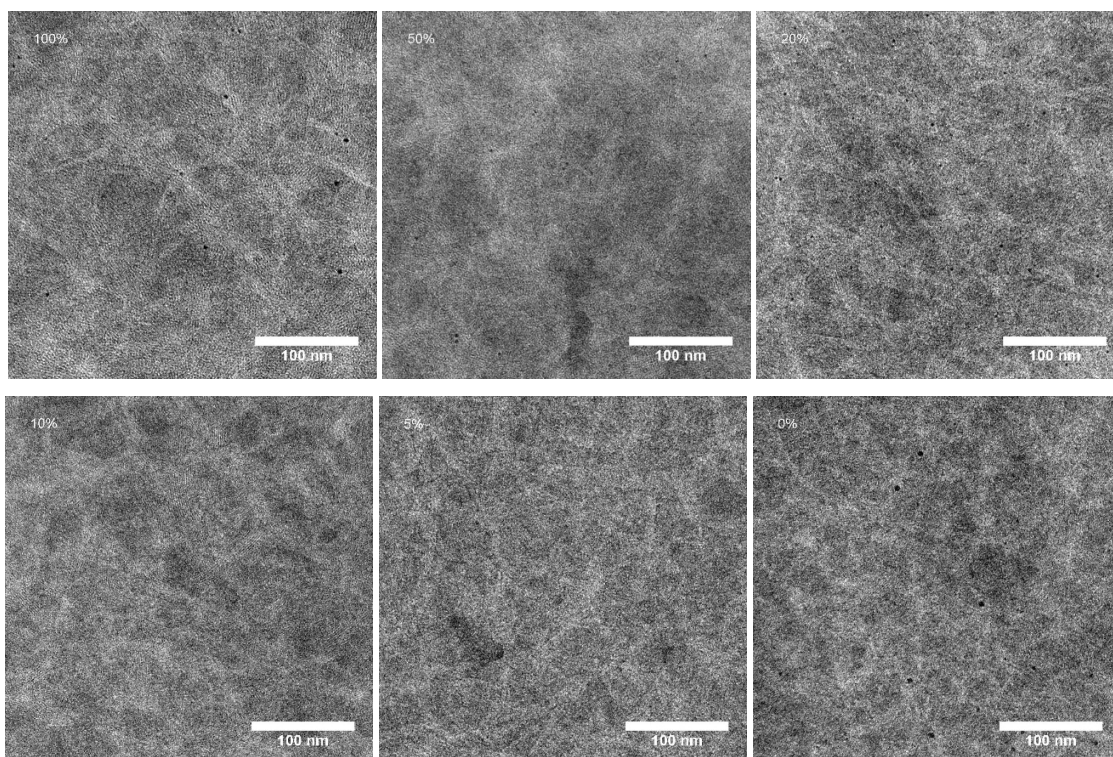


Fig. S4. TEM images of smaller scales of the polymer blends. First row: 100%, 50% and 20% siloxane polymers, second row 10%, 5% and 0% siloxane polymers.

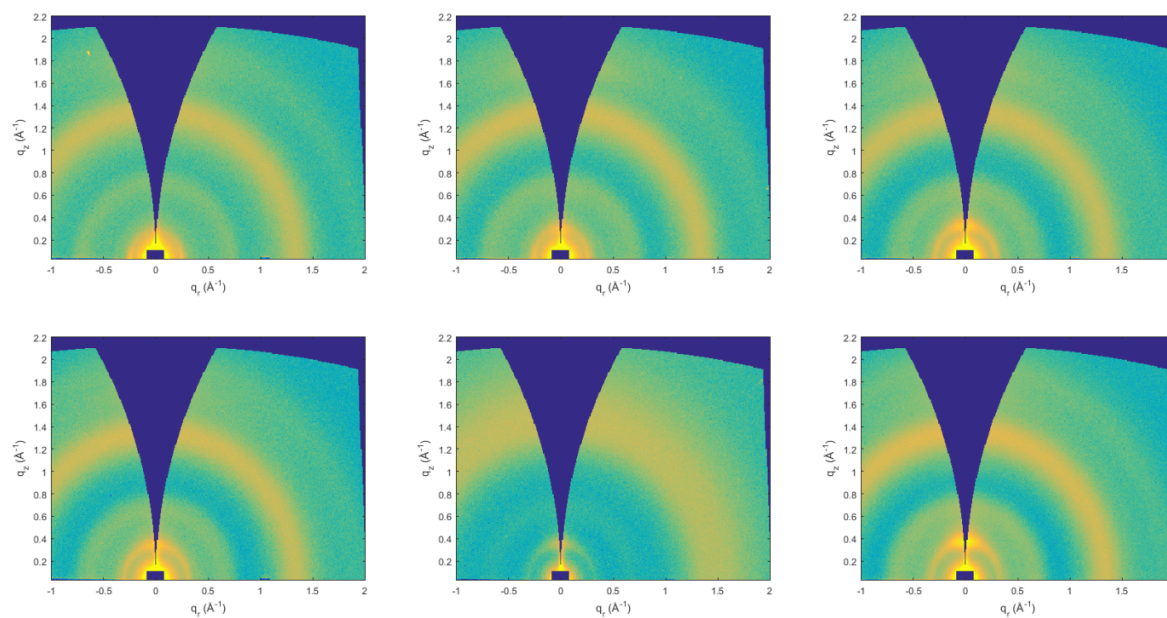


Fig. S5. Grazing incidence wide angle X-ray scattering of the polymer blends. First row: 100%, 50% and 20% siloxane polymers, second row 10%, 5% and 0% siloxane polymers.

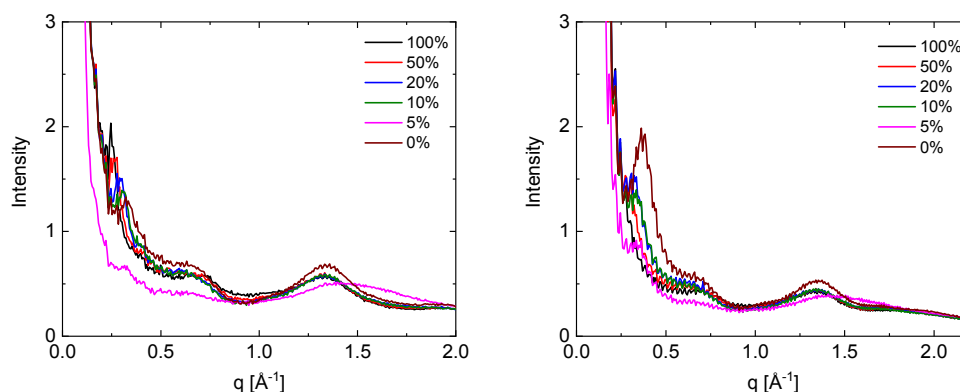


Fig. S6. In-plane and out-of-plane line cuts extracted from the GIWAXS analysis.

Supplemental discussion on GIWAXS

In Fig. S5 a change of edge-on to face-on orientation with increasing siloxane content can be seen. To further investigate this change, line cuts of the (100) peaks, normalized at 180° , were plotted over the radial angle (Fig S7). Here small angle approximation is valid and during the line cut analysis no further Fraser correction is made. If fibre symmetry with respect to the normal of the film plane is assumed, then we have complete information with respect to the orientation of 100 planes. From this plot a general decreasing trend of the intensity at 90° and 270° (in plane direction) with decreasing siloxane content is visible. This validates the notion that the orientation changes.

To roughly quantify this change, a pole figure analysis was carried out.⁵ The intensity between 90° – 135° and 225° – 270° (A_{xy}) was integrated and compared to the integrated intensity between 145° – 215° (A_z), ranges which correspond to the face-on and edge-on crystallites respectively. By taking the ratio A_{xy}/A_z , a relative ratio between the face-on and edge-on orientation could be calculated. As can be seen in Fig. S8, this ratio increases with increasing siloxane content, indicating a change in orientation from mostly edge-on (0% siloxane), through mixed orientation (50% siloxane), to mostly face-on (100% siloxane).

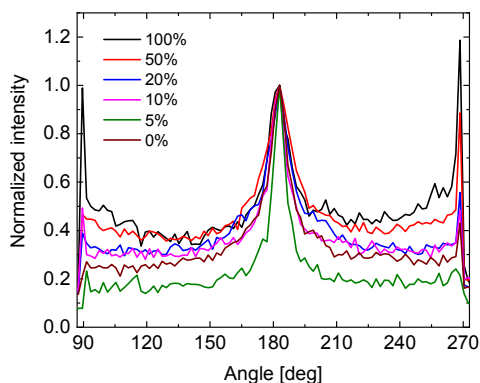


Fig. S7. The (100) peak over all angles.

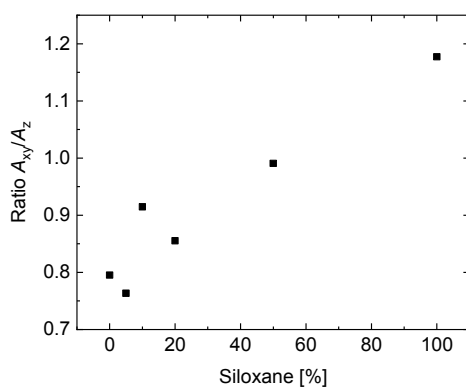


Fig. S8. The ratio A_{xy}/A_z in function of the siloxane content, with A_{xy}/A_z the ratio of face-on to edge-on orientation.

Supplementary discussion on stability

To preliminarily assess the stability of these materials and devices, solar cells were produced from polymers that were stored for >1 year under ambient conditions in the dark. Devices were produced as the described in the materials and methods section and stored in a nitrogen atmosphere to prevent oxidation of the electrodes. Devices were measured directly after fabrication and after 6 months storage. The results are shown in Table S1. As can be seen, the initial performances of the 5% and 50% siloxane polymers are somewhat lower than those in Table 2, mainly due to a decrease in J_{sc} and FF. The 100% siloxane polymer performs however the same, which suggests that the siloxane content does not induce faster degradation of the material. This notion becomes especially clear when looking at the aged devices. Rather surprisingly, the performance increased for all the cells, mainly in V_{oc} and FF, but also in J_{sc} in the case of the 5% and 50% siloxane polymers. This increase in PCE for the 5% and 50% siloxane polymers

brings them closer to the values in Table 2, thus definitely excluding material degradation as the cause for the lower initial performance. This also suggests that the devices and blend layers are quite stable over longer periods of time.

Table S1. Photovoltaic performance of PDPPTPT:[70]PCBM 1:2 (w/w) blends after fabrication and after aging for 6 months.^a

Siloxane fraction	J_{sc} [mA/cm ²]	V_{oc} [V]	FF	PCE[%]
0%	15.3 (15.3)	0.77 (0.77)	0.59 (0.58)	6.9 (6.8)
0%, aged	15.1 (14.9)	0.78 (0.78)	0.61 (0.60)	7.2 (7.0)
5%	13.3 (13.4)	0.78 (0.76)	0.58 (0.54)	6.0 (5.5)
5%, aged	13.8 (14.0)	0.80 (0.79)	0.66 (0.64)	7.3 (7.1)
50%	8.8 (8.8)	0.73 (0.71)	0.49 (0.48)	3.2 (3.0)
50%, aged	10.0 (10.1)	0.81 (0.81)	0.64 (0.64)	5.2 (5.2)
100%	7.7 (7.7)	0.81 (0.79)	0.57 (0.53)	3.5 (3.2)
100%, aged	7.2 (6.9)	0.83 (0.83)	0.58 (0.57)	3.4 (3.3)

^a Best cells are shown, numbers between parentheses refer to the average over 4 cells

References

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