Electronic Supplementary Material (ESI) for Polymer Chemistry

SUPPORTING INFORMATION

Thermally reactive Thiazolo[5,4-*d*]thiazole based copolymers for high photochemical stability in polymer solar cells

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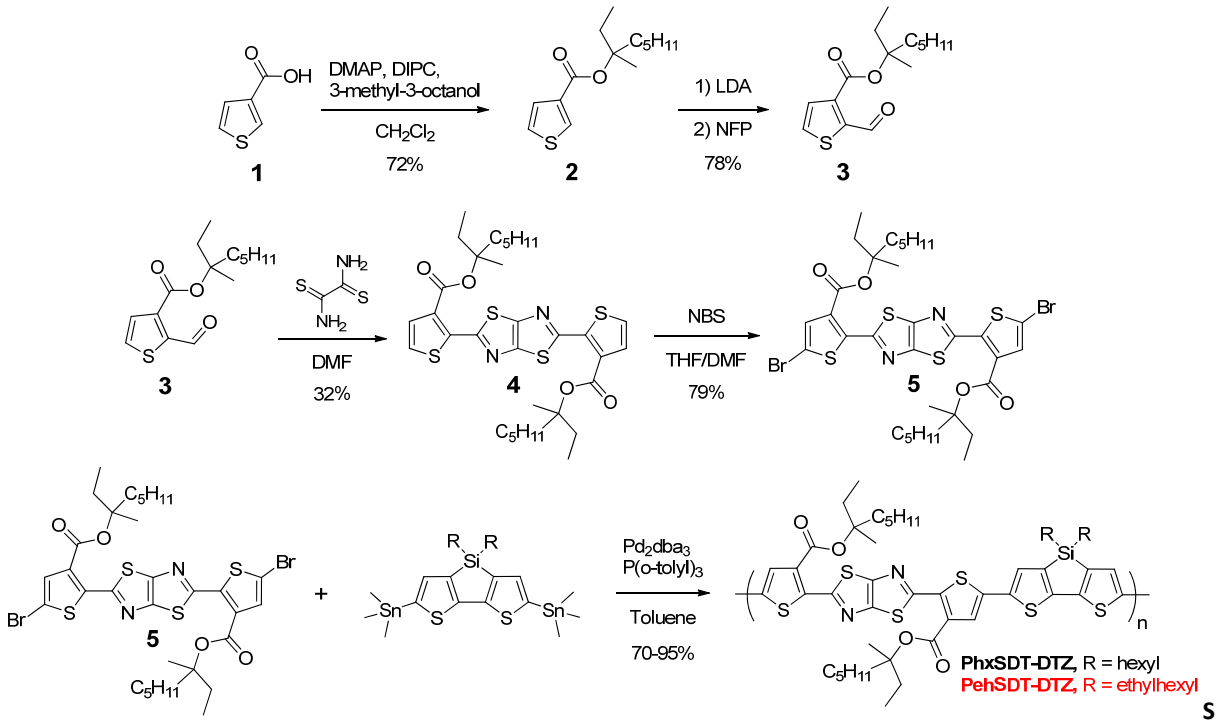
General experimental details

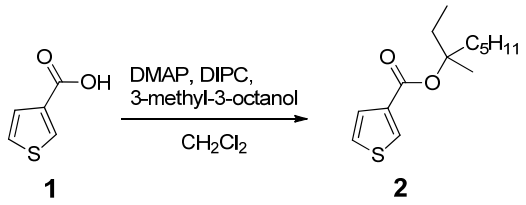
General methods, instrumentation and materials. Molecular weights were determined using size exclusion chromatography in HPLC-grade chloroform against polystyrene standards on a KNAUER chromatograph with a refractive index detector and a diode array UV-vis detector. UV-vis absorption spectra were measured with a Perkin-Elmer Lambda 900 spectrometer Atomic Force Microscopy (AFM) imaging was performed on a N8 NEOS (Bruker Nano GmbH, Herzogenrath, Germany) operating in an intermittent contact mode using PPP-NCLR cantilevers (NANOSENSORS, Neuchatel, Switzerland). Images were recorded at a scan speed of 1 line s^{-1}. Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) patterns were obtained from polymer/PCBM thin films, deposited by spin coating a 1:2 blend of the polymer (**PhxSDT-DTZ** or **PehSDT-DTZ**) and PCBM dissolved in 1,2-dichlorobenzene on a silicon wafer substrate, using the custom designed GIWAXS setup described by Apitz *et al.*[1] By orienting the substrate surface at or just below the critical angle for total reflection with respect to the incoming X-ray beam (~0.2°), scattering from the deposited film is maximized with respect to scattering from the substrate. Unless stated otherwise all reagents and solvents were obtained from Aldrich and used without further purification. Dichloromethane, THF and toluene were dried with molecular sieves (3 Å) and used directly without filtration or distillation. NBS was recrystallized from water and dried at 70 °C in vacuum. Evaporation was performed on a rotary evaporator at 40 °C. NMR spectra were obtained on a Bruker 250 MHz or 500 MHz spectrometer. 3-methyl-3-octyl thiophene-3-carboxylate (**2**), 4,4-dihexyl-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene and 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene were prepared according to literature procedures[2,3] or slight modifications thereof.

[1] Apitz, D.; Bertram, R.P.; Benter, N.; Hieringer, W.; Andreasen, J.W.; Nielsen, M.M.; Johansen, P.M.; Buse, K. *Phys. Rev.* **2005**, *E 72*, 036610.
[2] Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J.Am.Chem.Soc.* **2006**, *128*, 9034-9035
[3] Helgesen, M.; Bjerring, M.; Nielsen, N. C.; Krebs, F. C. *Chem. Mater.* **2010**, *22*, 5617-5624.

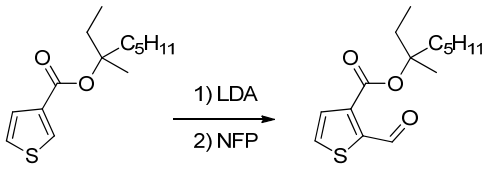
Synthetic procedures and characterization data



cheme S1. Synthetic steps involved in the preparation of the polymers

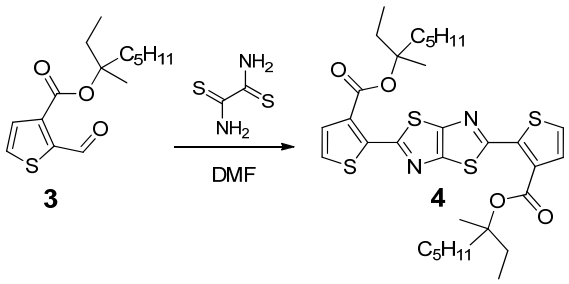


3-methyl-3-octyl thiophene-3-carboxylate (2): A mixture of thiophene-3-carboxylic acid (**1**) (5 g, 39 mmol), DMAP (5.2 g, 43 mmol) and 3-methyl-3-octanol (7.5 ml, 43 mmol) in dry methylene chloride (50 ml) was stirred at room temperature under argon for 15 min. *N,N'*-diisopropylcarbodiimide (6.7 ml, 43 mmol) was added and the reaction mixture was heated to 40 °C and stirred for 24 hours. After cooling to room temperature the reaction mixture was concentrated on celite in vacuum. Dry column chromatography (silica gel 15-40 µm, eluted with EtOAc/heptane, gradient 0-3% EtOAc) afforded **2**. Yield: 7.1 g (72 %), colourless oil. ^{1}H NMR (250 MHz, $CDCl_3$) δ = 8.00 (dd, J = 3.0 Hz, J = 1.1 Hz, 1H), 7.46 (dd, J = 5.1 Hz, J = 1.1 Hz, 1H), 7.26 (dd, J = 5.1 Hz, J = 3.0 Hz, 1H), 2.08 – 1.73 (m, 4H), 1.50 (s, 3H), 1.39 – 1.23 (m, 6H), 0.96 – 0.84 (m, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 161.93, 135.68, 131.78, 127.96, 125.56, 85.89, 38.05, 32.18, 31.13, 23.43, 23.33, 22.56, 14.00, 8.07.



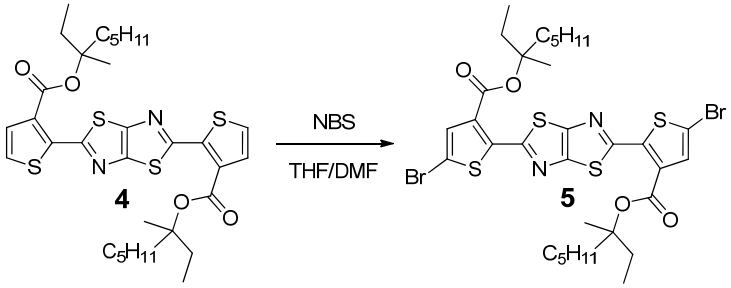
2 **3**

3-methyl-3-octyl 2-formylthiophene-3-carboxylate (3): 10 ml dry THF was cooled to -10 °C under argon followed by addition of 10 ml *n*-butyllithium (1.6 M in hexane). Then a solution of 2.4 ml diisopropylamine and 7.6 ml dry THF was added slowly and the reaction mixture was stirred for 30 min. 26 ml (13 mmol) of the freshly prepared solution of lithium diisopropylamine was added slowly to a cooled solution (-78 °C) of **2** (3 g, 12 mmol) in dry THF (30 ml). The reaction mixture was stirred for 1 hour at -78 °C under argon followed by addition of *N*-formylpiperidine (NFP, 3.9 ml, 35 mmol). The reaction mixture was allowed to warm to room temperature over 2 hours. Water was added to the reaction mixture followed by extraction with ether. The combined organic phase was dried over magnesium sulfate, filtered and concentrated in vacuum. Dry column chromatography (silica gel 15-40 µm, eluted with EtOAc/heptane, gradient 0-5% EtOAc) afforded **3**. Yield: 2.6 g (78 %), light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.61 (d, *J* = 1.2 Hz, 1H), 7.63 (dd, *J* = 5.1 Hz, 1.2 Hz, 1H), 7.54 (d, *J* = 5.1 Hz, 1H), 2.11 – 1.84 (m, 4H), 1.57 (s, 3H), 1.40 – 1.27 (m, 6H), 0.99 – 0.88 (m, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) *δ* = 184.93, 161.01, 146.77, 138.76, 132.44, 131.21, 88.22, 37.88, 32.11, 31.01, 23.49, 23.39, 22.54, 14.00, 8.13.

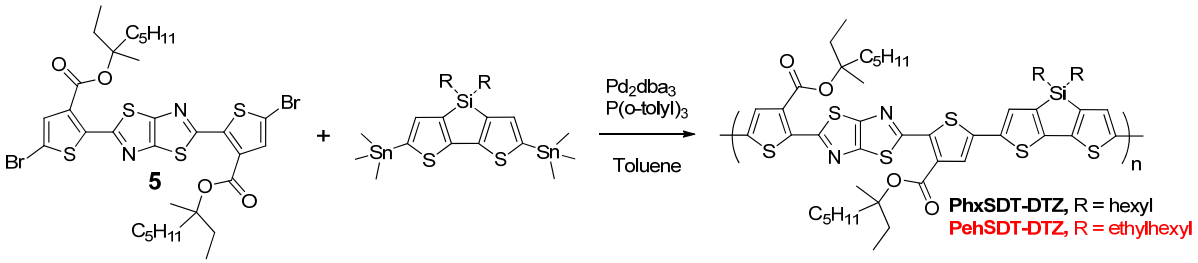


3 **4**

bis(3-methyl-3-octyl) 2,2'-(thiazolo[5,4-d]thiazole-2,5-diyl)bis(thiophene-3-carboxylate) (4): A solution of **3** (2.9 g, 10 mmol) and dithiooxamide (568 mg, 4.7 mmol) in *N,N*-dimethylformamide (12 mL) was heated to 125 °C for 5 h and then cooled down to room temperature. The reaction mixture was poured into water and extracted with dichloromethane. The combined organic phase was dried over magnesium sulfate, filtered and concentrated in vacuum. Dry column chromatography (silica gel 15-40 µm, eluted with toluene/heptane, gradient 0-100% toluene) followed by recrystallization from ethanol afforded **4** as a dark orange solid. Yield: 964 mg (32 %). M_p = 101-102 °C. ^{1}H NMR (500 MHz, $CDCl_3$) *δ* = 7.47 (d, *J* = 5.4 Hz, 2H), 7.38 (d, *J* = 5.4 Hz, 2H), 2.10 – 1.81 (m, 8H), 1.57 (s, 6H), 1.40 – 1.26 (m, 12H), 0.98 – 0.87 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 162.36, 160.47, 153.03, 143.17, 131.08, 130.58, 127.14, 87.44, 37.95, 32.17, 31.06, 23.44, 23.38, 22.58, 14.04, 8.17. HRMS-ES+: *m/z* calcd for $C_{32}H_{43}N_2O_4S_4$ $[M + H]^+$, 647.2112; found, 647.2106.



bis(3-methyl-3-octyl) 2,2'-(thiazolo[5,4-d]thiazole-2,5-diyl)bis(5-bromothiophene-3-carboxylate) (5): To a solution of **4** (900 mg, 1.4 mmol) in 40 ml THF/DMF (2:1) was added NBS (545 mg, 3.1 mmol) and one drop acetic acid. The resulting mixture was then stirred at room temperature for 48 hours. During this period the reaction was monitored by TLC and additional portions of NBS (5 x 170 mg) were added until the conversion was complete. The mixture was poured into brine and extracted several times with dichloromethane. The combined organic phase was dried ($MgSO_4$), filtered and concentrated in vacuum. Dry column chromatography (silica gel 15-40 µm, eluted with toluene/heptane, gradient 0-50% toluene) afforded **5** as an orange solid. Yield: 882 mg (79 %). M_p = 187-188 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39 (s, 2H), 2.10 – 1.83 (m, 8H), 1.57 (s, 6H), 1.42 – 1.28 (m, 12H), 0.98 – 0.88 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 161.25, 159.50, 153.46, 145.15, 132.81, 130.61, 115.37, 88.06, 37.86, 32.14, 31.03, 23.44, 23.38, 22.56, 14.03, 8.18. MS-ES+: *m/z* calcd for $C_{32}H_{41}Br_2N_2O_4S_4$ $[M + H]^+$, 803.03; found, 803.28.



PhxSDT-DTZ: **5** (200 mg, 0.25 mmol), 4,4-dihexyl-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene (171 mg, 0.25 mmol), Pd_2dba_3 (11 mg, 0.012 mmol) and tri-(o-tolyl)phosphine (19 mg, 62 mmol) was mixed in dry degassed toluene (6 ml). The reaction mixture was heated to reflux for 48 hours under argon. After cooling to room temperature the mixture was poured into 100 ml methanol and the polymer was allowed to precipitate. The polymer was filtered and purified by Soxhlet extraction using methanol, hexane and chloroform. The chloroform phase was concentrated to a smaller volume in vacuum and precipitated in methanol (1:10). Filtration and drying in vacuum afforded **PhxSDT-DTZ** as a dark blue solid. Yield: 237 mg (95 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.55 – 6.83 (br, 4H), 2.44 – 0.68 (br, 64H). SEC ($CHCl_3$): M_w = 32400, M_n = 9500, PDI = 3.4.

PehSDT-DTZ: Prepared with the same procedure as for **PhxSDT-DTZ** using the monomers **5** and 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophene. Yield: 187 mg (70 %), dark blue solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44 (br s, 1H), 7.18 (s, 1H), 6.91 (s, 2H), 2.49 – 0.60 (m, 72H). SEC ($CHCl_3$): M_w = 30800, M_n = 14000, PDI = 2.2

Figure S1. ^{1}H-NMR Spectrum of **4** in $CDCl_3$

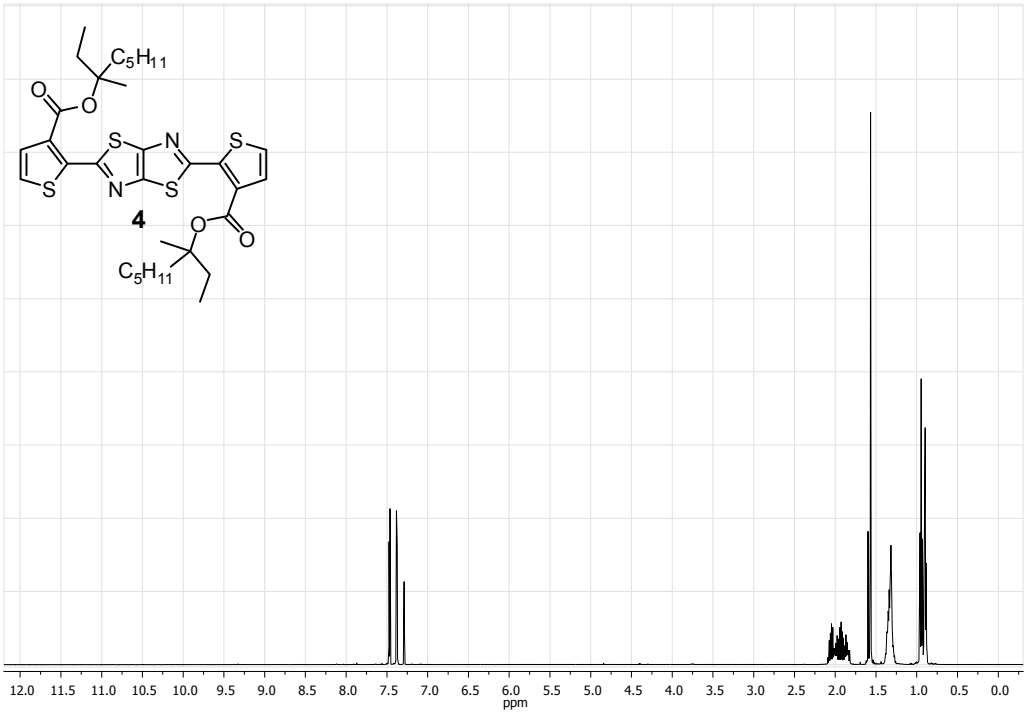


Figure S2. ^{13}C-NMR Spectrum of **4** in $CDCl_3$

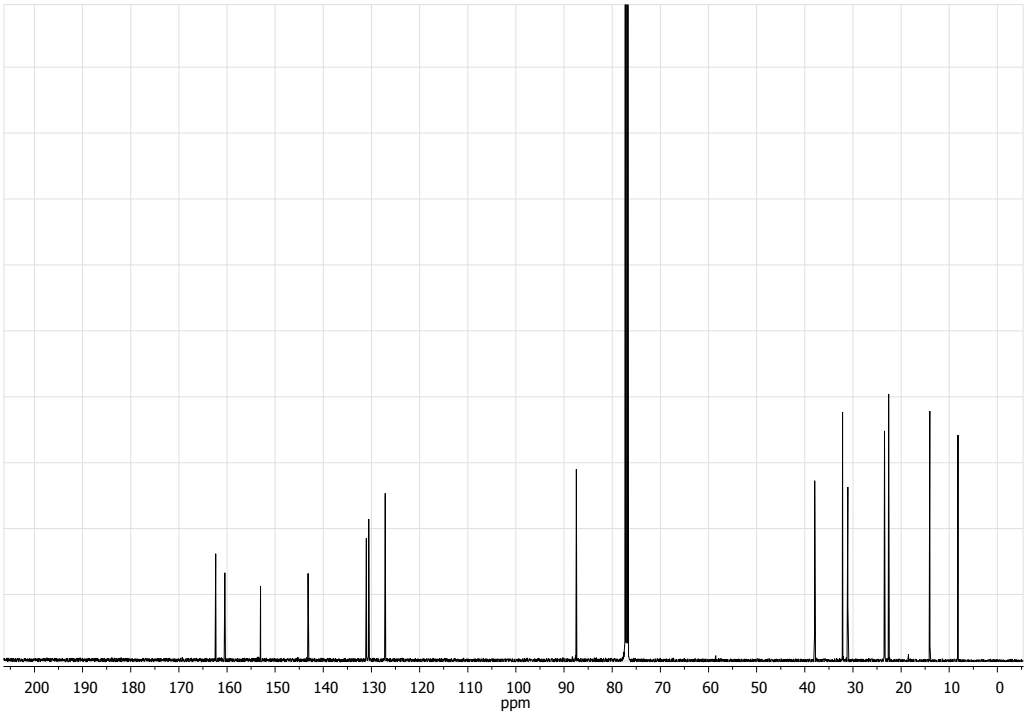


Figure S3. ^{1}H-NMR Spectrum of **5** in $CDCl_3$

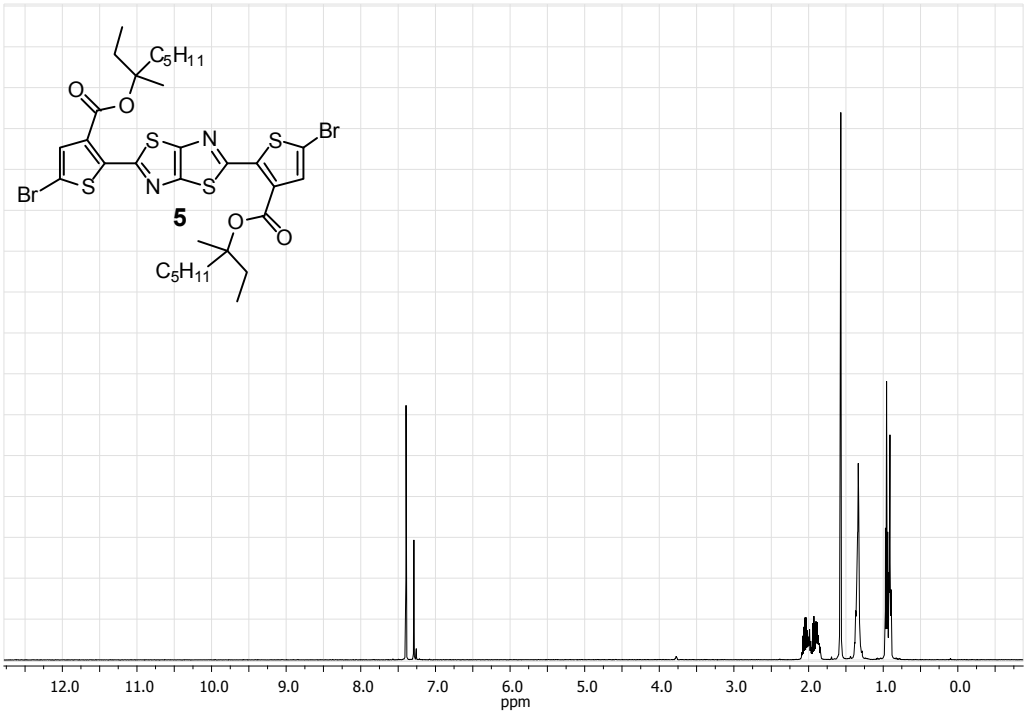
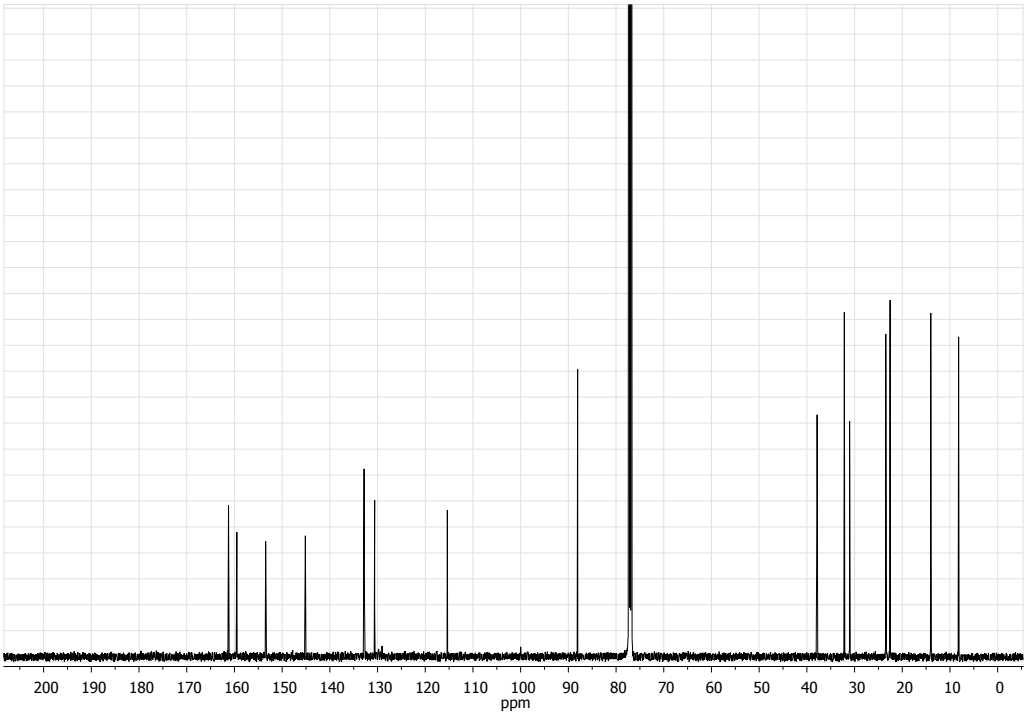
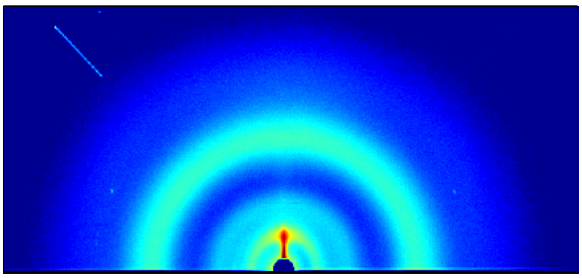


Figure S4. ^{13}C-NMR Spectrum of **5** in $CDCl_3$



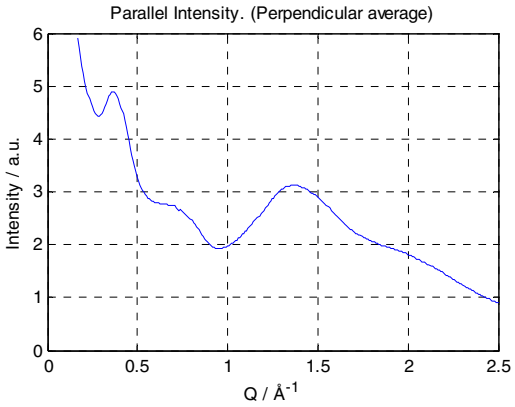
GIWAXS data

PhxSDT-DTZ/PCBM thin film

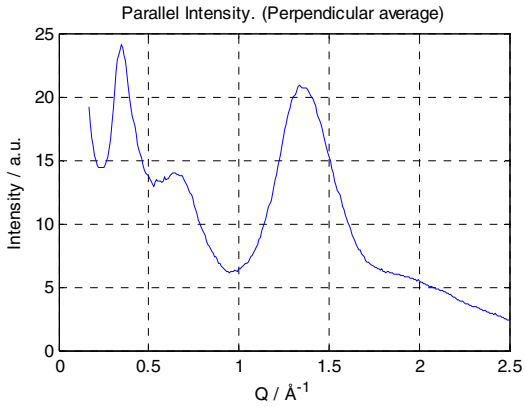


Gaussian fit:
Centre = 0.37054
Amplitude = 79.8516
Sigma = 0.038053 (FWHM = 0.089608)
Offset = 196.708
Slope = -328.7948

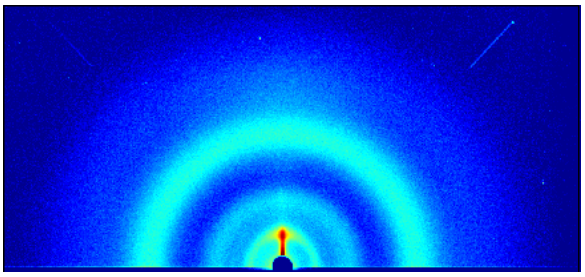
Qz



Qxy



PhxSDT-DTZ*/PCBM thin film



Gaussian fit:
Centre = 0.36515
Amplitude = 19.8507
Sigma = 0.032202 (FWHM = 0.075831)
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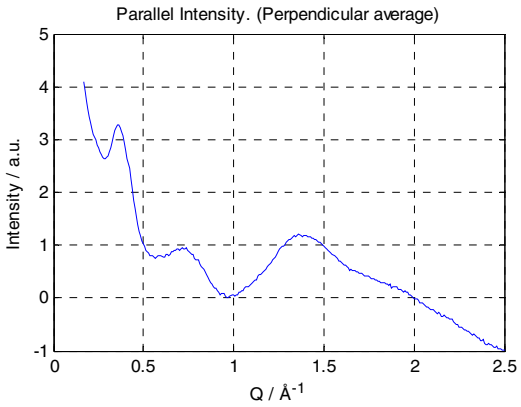
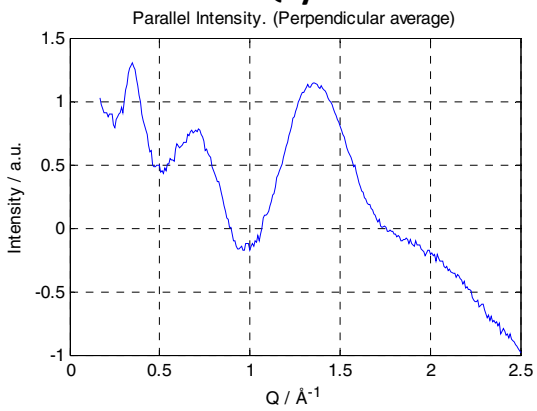
Slope = -72.1281

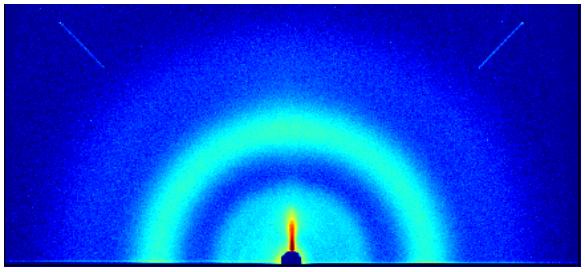
Qz



Qxy

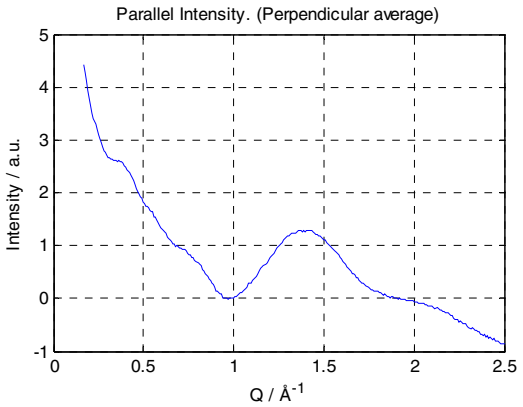


PehSDT-DTZ/PCBM thin film



Gaussian fit:
Centre = 0.34899
Amplitude = 12.5659
Sigma = 0.08092 (FWHM = 0.19055)
Offset = 4.4928
Slope = -0.83085

Qz



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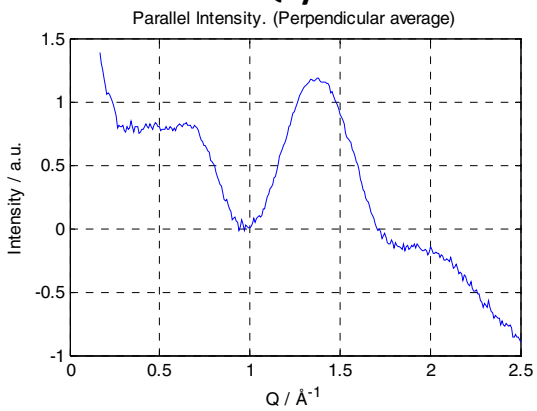

PehSDT-DTZ*/PCBM thin film