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Supporting Information

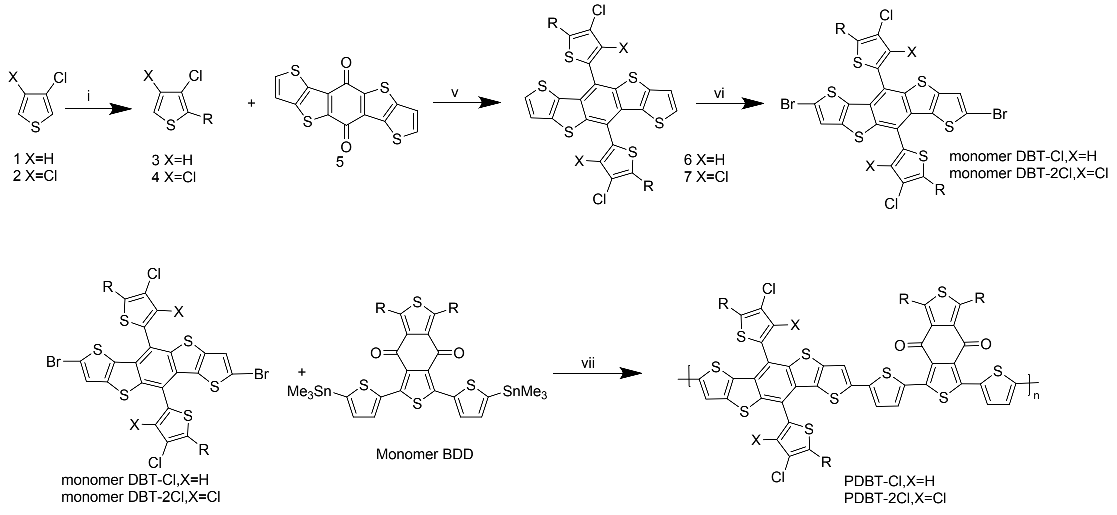
Significant Influence of Halogenation to Energy Levels and Molecular Configurations for DTBDT-based Polymers Solar Cells

Jiaming Huang[a,b,†], Lingchao Xie [a,†], Ling Hong[a,b], Lirong Wu[a] , Yufang Han[a,b], Tingting Yan[a,b], Jianqi Zhang[c], Liqiang Zhu[a], Zhixiang Wei[c] and Ziyi Ge [a,b,*]

Experiment Section

Materials: IT-4F, PDINO were purchased from Solarmer Materials (Beijing) Inc and were used without any further purification. Other chemicals were purchased from Sigma-Aldrich, Inc.

Synthesis Procedures of PDBT-Cl, PDBT-2Cl



compound 3: Synthesizing according to previous literiture[1].

compound 4: To a dry THF (100 ml)solution of compound 2 (10g, 0.065 mol), 78 ml LDA (1M in hexane 0.078mol) was added dropwise at -78 °C. After that, 2-Ethylhexyl bromide (16.24g, 0.078mo) was added and the mixture was stirred at rt. overnight. Then, the mixture was quenched with water, extracted with $CHCl_2$ (100ml×3). The organic layer dried over anhydrous $MgSO_4$.Colourless liquid was steaming through reduced pressure distillation fraction. ^{1}H NMR (400 MHz, CDCl3, δ/ppm): 7.04 (s, 1H), 2.73 (d, J = 7.0 Hz, 2H), 1.69 – 1.59 (m, 1H), 1.33 (dd, J

= 17.1, 10.3 Hz, 8H), 0.89 (t, J = 7.3 Hz, 6H).

compound 6: To a THF (50 mL) solution of compound 3 (2.40 g, 10.4 mmol) , 5.4 mL (13.4 mmol) of n-BuLi (2.5 M in hexane) was added dropwise at –20 °C. After that, the mixture was stirred at 50°C for 1 h to lithiated completely. And it was stirred at 50 °C for one more hour after compound 5(1.10 g, 3.4 mmol) was added. Furthermore, tin chloridedihydrate (5.0 g) in 20 mL of HCl (10%) was added when reaction was at r.t. for one hour. The mixture was quenched with water, extracted with $CHCl_3$ (100ml×3). The organic layer dried over anhydrous $MgSO_4$. The light yellow powder was gained by using column chromatography on silica gel while n-hexane was treaded as eluent. Yield: 2.16g (84%). ^1H NMR (400 MHz, $CDCl_3$, δ/ppm): 7.46 (d, 2H), 7.26 (d, 2H), 7.14 (d, 2H), 2.81 (d,4H), 1.80 (m, 2H), 1.6–1.4 (m, 16H), 1.06–0.88 (t, 12H).

compound 7 refers to compound 6 above.^1H NMR (400 MHz, $CDCl_3$, δ/ppm) 7.48 (dd, J = 5.2, 1.7 Hz, 1H), 7.28 (d, J = 5.2 Hz, 1H), 2.94 (m, 2H), 1.80 (d, J = 5.7 Hz, 1H), 1.53 – 1.30 (m, 8H), 0.96 (m, 6H).

DTBDT-Cl: To a solution of compound 6 (0.91g, 1.2 mmol) in $CHCl_3$ and acetic acid of total 20 ml (V: V= 1: 1), N-bromosuccinimide (0.13 g, 3.6 mmol) was added in one-off at 0 °C. The mixture was stirred for 24 h and then stopping by pouring into moderate water. The organic layer was extracted with $CHCl_3$ (50 ml×3), dried over anhydrous $MgSO_4$. The coarse product was obtained by evaporating the solvent and purified as the same way of column chromatography. Finally, light yellow powder was precipitated with CH_3OH to purification. Yield: 0.97 g (88%). ^1H NMR (400 MHz, $CDCl_3$, δ/ppm) 7.46 (d, 2H), 7.12 (d, 2H), 2.81 (d,4H), 1.80 (m, 2H), 1.6–1.4 (m, 16H), δ1.06–0.88 (t, 12H).

DTBDT-2Cl: The synthesis of monomer DBT-2Cl refers to monomer DBT-Cl above. ^1H NMR

(400 MHz, $CDCl_3$, δ/ppm): 7.28 (s, 1H), 2.94 (m, 1H), 1.80 (s, 1H), 1.53 – 1.27 (m, 4H), 1.04 – 0.89 (m, 3H). ESI-TOF-MS: m/z [M+] calcd for $C_{38}H_{36}Br_2Cl_4S_6$, 986.8212; found: 986.8276.

PDBT-Cl：To a 10ml reaction tube, monomer DBT-Cl (60 mg, 0.067 mmol), monomer BDD (61.21 mg,0.067), triphenylphosphine palladium (4 mg) were dissolved in ultra-dry chlorobenzene. In a pure helium atmosphere，the mixture was stirred in 100°C for 12 h. Then, polymer was added in methanol dropwisely and precipitated. The precipitate was collected and extracted in a Soxhlet extractor with methanol, n-hexane and chloroform. The black solid was obtained by methanol sedimentation. M_n = 111.96 kDa, M_w = 154.48 kDa, PDI = 1.38

PDBT-2Cl: The synthesis of PDBT-2Cl refer to PDBT-Cl. M_n = 99.7 kDa, M_w = 142.57 kDa, PDI = 1.43.

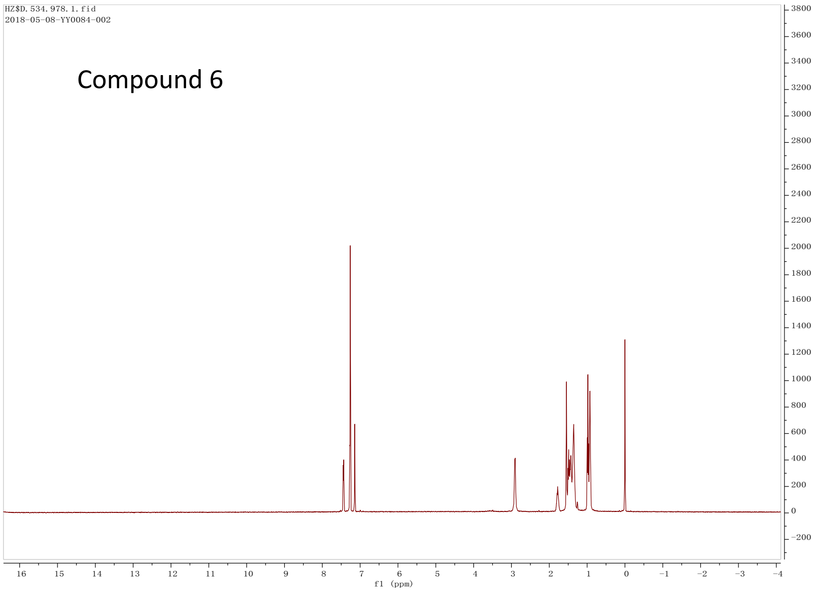
Characterization and Measurement

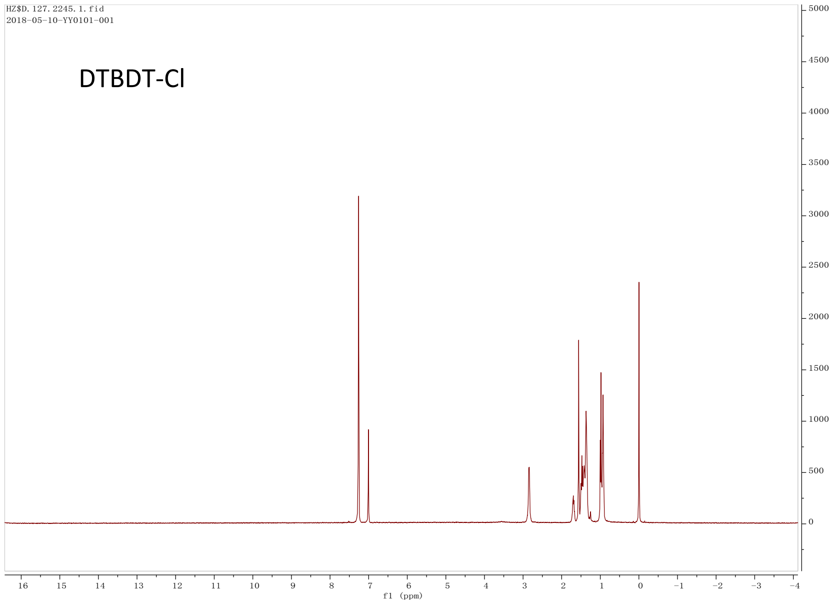
Chemical structure of obtained polymer and other products were identified by ^{1}H NMR (Avance DPX-300) using $CDCl_3$ as solvent. The molecular weights of the polymers were measured by Viscotek GPC systems from Malvern Instruments. The energy levels of polymers are measured by cyclic voltammetry (CV) in CHI660C electrochemical workstation from Chenhua Inc. UV-vis absorption spectra were measured by a Perkin-Elmer Lambda 950 spectrophotometer. The AFM images were investigated by a Veeco Dimension 3100V atomic force microscope.

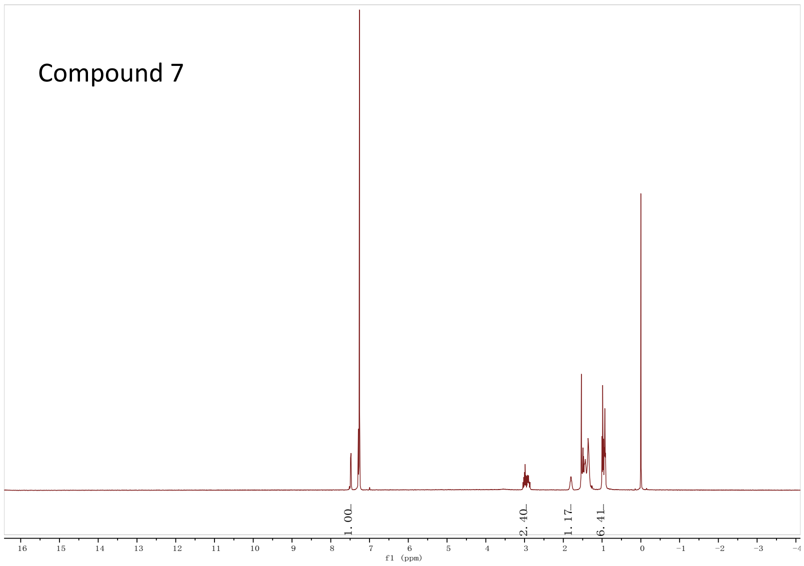
Device Fabrication and Characterization

The devices configuration isITO glass/PEDOT: PSS/active layer/PDINO/Al. The ITO glass as anode was cleaned by distilled water, acetone, isopropanol in ultrasonic cleaner. The PEDOT:PSS aqueous solution was filtered through a 0.45 nm filter and spin-coated at 3000 rpm for 1 min onto the treated ITO substrate after treated in ultraviolet ozone chamber and annealed at 130° C for 10 min. The solution of active layer prepared by solving donor and acceptor in chloroform. 1,8-diiodoctane (DIO) was used as additive. The active layer was spin-coated onto the PEDOT: PSS at

2000 rpm for 1 min and then thermal annealing at 100° C for 10 min. The PDINO was spin-coated onto the active layer at 3000 rpm for 1 min. Al was deposited about 100 nm. Simulated solar light (100 mW cm2 AM 1.5G) provided by a Newport-Oriel® Sol3A 450 W solar simulator was used to measure the photovoltaic characteristics of the devices under simulated solar light (100 mW cm^2 AM 1.5G). The EQE spectra were determined by a Newport-Oriel® IQE 200™ which was calibrated by a standard Si/Ge solar cell. The thickness of the active layer was investigated using a computer-controlled Dektak 150 Veeco.




HZ$D.127.2245.1.fid
2018-05-10-YY0101-001
DTBDT-Cl
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)


Compound 7
1.00
2.40
1.17
6.41
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)

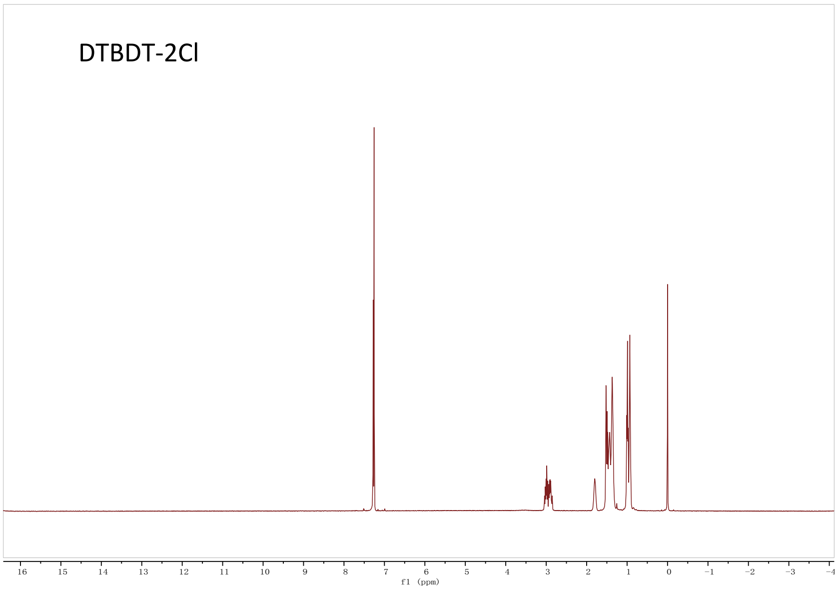


Figure S1 ^{1}H NMR spectra of products

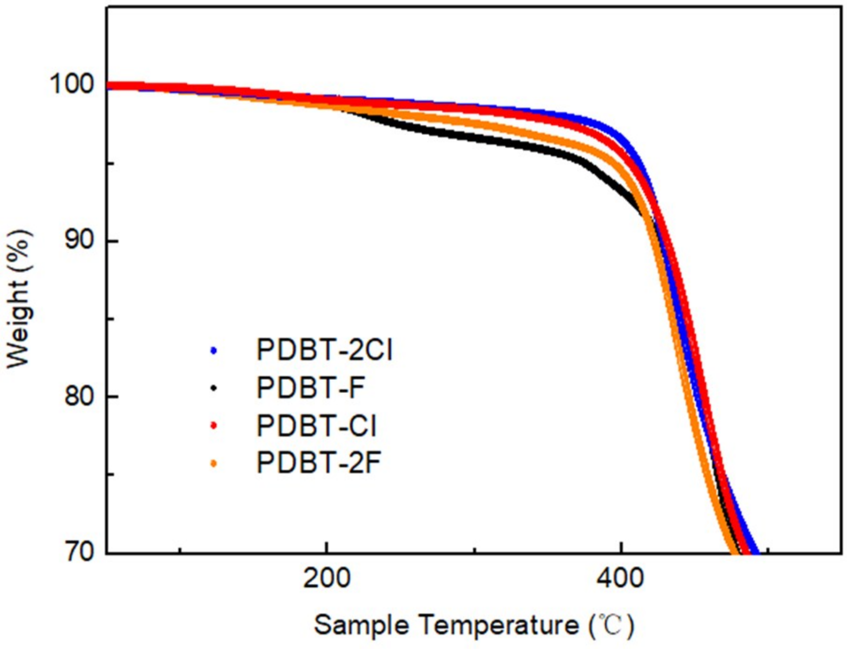


Figure S2 TG curves of polymers

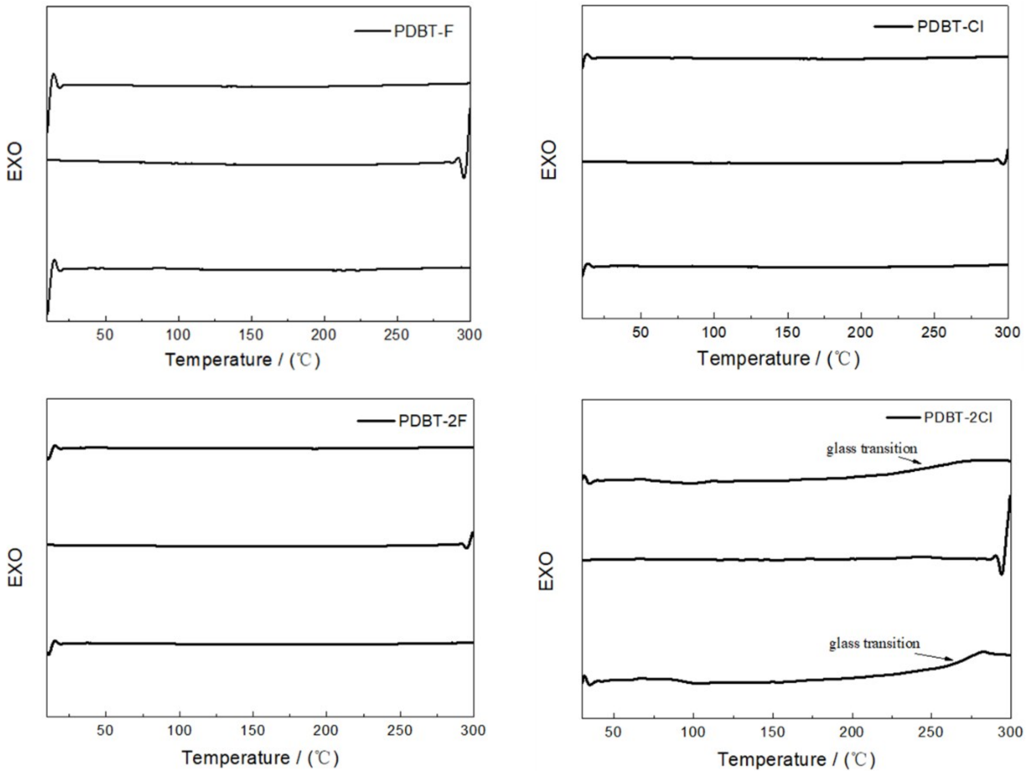


Figure S3 DSC plots of polymers

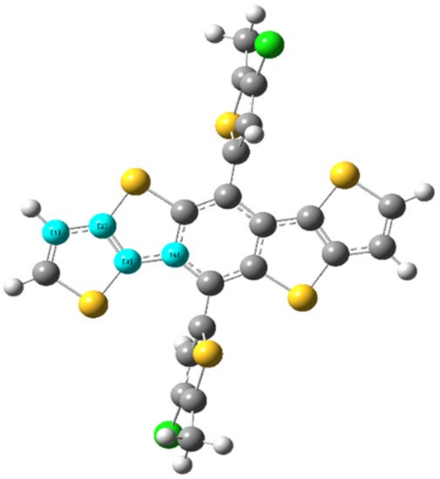


Figure S4 Planarity of DTBDT unit from DFT result (blue atoms)

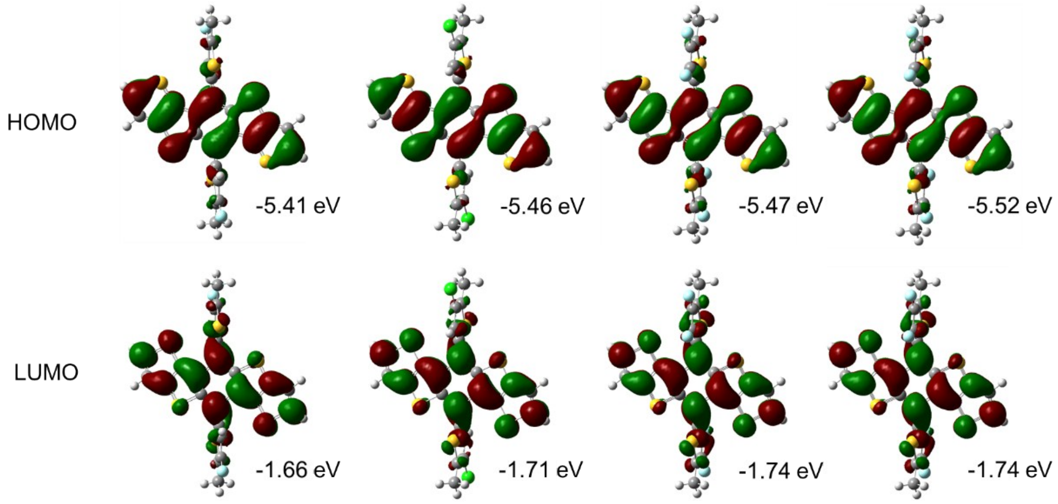


Figure S5 DFT results for energy levels of polymers

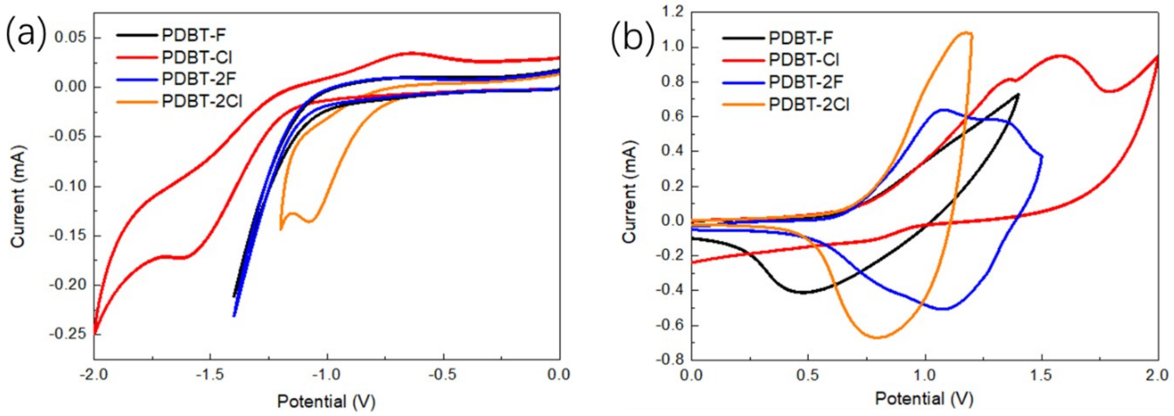


Figure S6 CV curves of polymers (left) reduction (right) oxidation

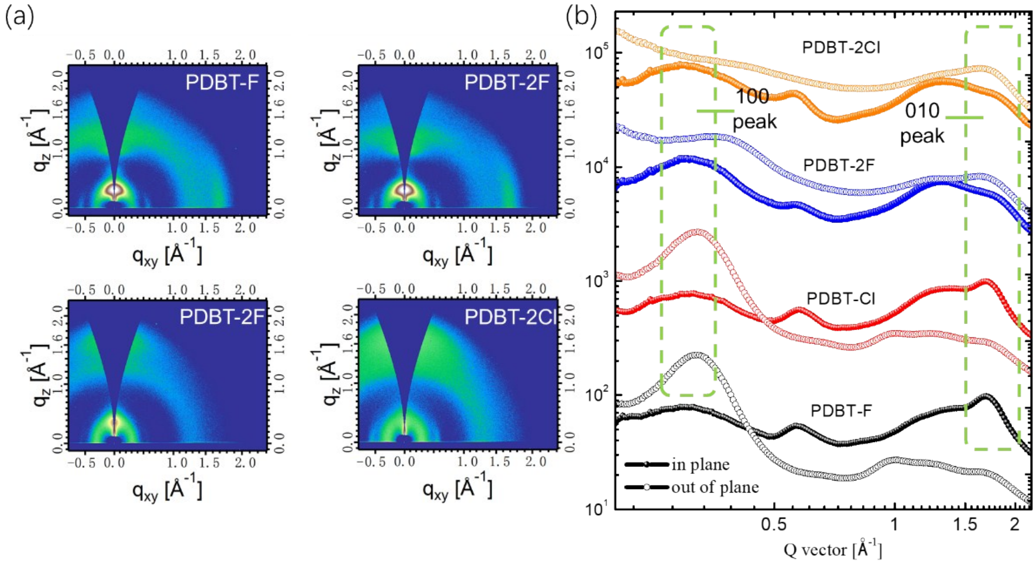


Figure S7 2D and 1D GIWAXS images of neat films of polymers

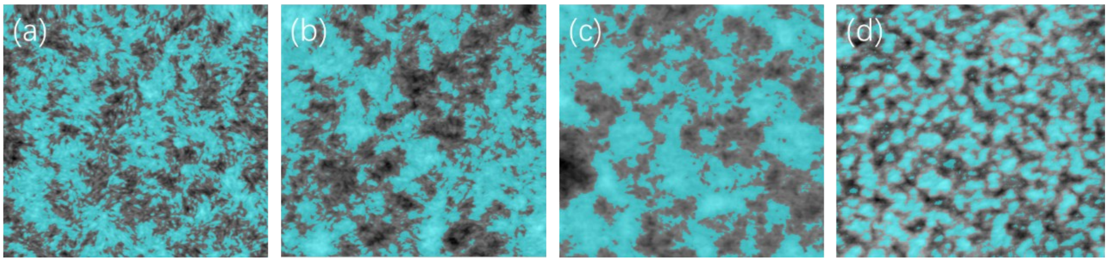


Figure S8 grain size analysis of AFM images (from Gwyddion software).

a) PDBT-F, b)-Cl, c)-2F and d)-2Cl

[1] S. Zhang, Y. Qin, J. Zhu, J. Hou, *Adv. Mater.* **2018**, 30, 1800868.