

Supporting information for:

Cyano substituted benzotriazole based polymers for use in organic solar cells

Abby Casey,^a Joshua Green,^a Pabitra Shakya-Tuladhar^a, Mindaugas Kirkus^a, Yang Han^{a,b} Thomas D. Anthopoulos^b and Martin Heeney^{a*}

^aDept. Chemistry and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, U.K.

^bDept. Physics and Centre for Plastic Electronics, Imperial College London, London SW7 2AZ, U.K

*E-mail: m.heeney@imperial.ac.uk

General:

All solvents and chemicals, were purchased from Sigma-Aldrich and used without further purification. 4,7-Dibromo-5,6-difluoro-2-(2-butyloctyl)-2H-benzotriazole (**1**) 2,6-bis(trimethyltin)-4,8-bis(5-(2-butyloctyl)thiophene-2-yl)-benzo[1,2-b;4,5-b']dithiophene (**BDT(T-BO)**) were purchased from SunaTec Inc. 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophene-2-yl)-benzo[1,2-b;4,5-b']dithiophene(**BDT(T-EH)**) was synthesised according to literature procedures.¹ Microwave reactions were performed in a Biotage initiator V 2.3 in constant temperature mode. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) spectrometers in chloroform-d or tetrachloroethane-d₂ solutions. Number-average (M_n) and weight-average (M_w) molecular weights were determined with an Agilent 1260 in chlorobenzene at 80°C using two PL mixed B columns in series and calibrated against polystyrene standards (EasiCal PS-1). UV-Visible absorption spectra were measured using a Shimadzu UV-1800 UV-Vis Spectrophotometer. 16.6 mg/dm³ polymer solutions in 1,2,4-trichlorobenzene (TCB) were used for solution spectra whilst 5 mg/ml polymer solutions in hot TCB were used to spin coat thin films at 2000 rpm for 60 seconds. Solutions and films were not de-oxygenated for these measurements. Cyclic voltammograms were recorded using a Metrohm Autolab PGStat101 Potentiostat/Galvanostat. The experimental set-up consisted of an Ag/Ag⁺ quasi reference electrode, a platinum wire counter electrode and an FTO working electrode. All measurements were carried out under argon at room temperature (~25°C). Measurements of the polymers were done on spun-cast films in anhydrous, degassed solutions of acetonitrile with tetrabutylammonium hexafluorophosphate (0.1M) electrolyte. Thin films were spin coated onto FTO on glass substrate from a hot 5 mg/ml TCB solution. A ferrocene internal standard was used to calibrate the results assuming the ferrocene/ferrocenium reference redox system is 4.8 eV below the vacuum level. Atomic force microscopy images were obtained with a Picoscan PicoSPM LE scanning probe in tapping mode under ambient conditions. Thin films of the polymer were coated under the same conditions as those used for OPV devices. DFT calculations were performed using the B3LYP hybrid functional and the 6-31g(d) basis set in the GAUSSIAN09 software package.^[1] Alkyl chains were replaced with a propyl group to simplify calculations and reduce computational time. Structures were optimized, and a frequency analysis performed. Potential energy scans were performed on the trimers using the redundant coordinate editor and scanning the indicated dihedral angle in 36 steps of 10° increments.

OPV device fabrication:

ITO-coated glass substrates were washed by ultrasonication in acetone and isopropyl alcohol then dried before undergoing an oxygen plasma treatment. A thin layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was spin-coated onto the substrate and dried at 150 °C for 30 min. The active layer was spin-coated from a blend of 1:2 (weight ratio) polymer:PC₆₁BM in 1,2,4-trichlorobenzene (TCB) onto the PEDOT:PSS layer. The active layer solution made from polymer **P1** had a total concentration of ~20 mg/mL whilst the solution made from **P2** had a total concentration of ~24 mg/mL. Solutions of **P1** were heated at 135 °C for 6 h then 90 °C overnight to ensure dissolution before spin-coating at 700 rpm. Solutions of **P2** were heated to 135 °C for 30 minutes then 65 °C overnight before spin-coating at 700 rpm. A Ca (30 nm)/Al (100 nm) cathode layer was then deposited by thermal evaporation under vacuum through a

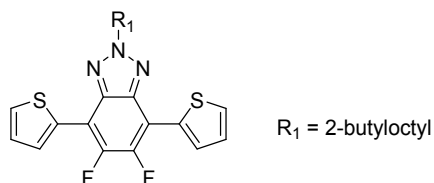
shadow mask to complete the BHJ cell. Current-voltage (J-V) characteristics were measured under AM1.5 solar illumination using a xenon lamp.

For devices using CuSCN as the hole transporting layer, a solution of CuSCN (20 mg/mL) in diethylsulfide was made and stirred until fully dissolved (~1h) under an inert nitrogen atmosphere (glovebox). The solution was then filtered with a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter. The filtered solution was spun at 2000 rpm for 60 s onto the cleaned ITO substrates and annealed at 100 $^{\circ}\text{C}$ for 30 min under an inert nitrogen atmosphere (glovebox). The active layers and cathodes were then deposited as described above.

Average efficiencies are based upon 6 devices, except **P1** (PEDOT:PSS; 3 devices), **P2-CB** (CuSCN HTL; 5 devices) and **P2-CF** (CuSCN HTL; 5 devices).

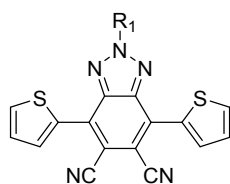
Synthesis:

5,6-difluoro-2-(2-butyloctyl)-4,7-di(thiophen-2-yl)-2H-benzotriazole



4,7-Bromo-5,6-difluoro-2-(2-butyloctyl)-2H-benzo[d][1,2,3]triazole **1** (0.940 g, 1.95 mmol), $\text{Pd}(\text{PPh}_3)_4$ (113 mg, 0.098 mmol), and a stirrer bar were added to a 20 mL high pressure microwave reactor vial. The vial was then sealed with a septum and flushed with argon before 2-thienylzinc bromide solution in THF (10 mL of a 0.5 M solution, 5.0 mmol) was added. The reaction was heated by microwave irradiation to 100 $^{\circ}\text{C}$ for 30 min. After cooling, the solvent was removed under reduced pressure and the crude product purified by column chromatography using ethyl acetate/hexane (5:95, v:v) to afford **2** as a yellow solid (900 mg, 0.185 mmol). Yield 94%; ^1H NMR (400 MHz, CDCl_3) δ 8.33 (dd, $J = 3.7, 1.1$ Hz, 2H), 7.55 (dd, $J = 5.1, 1.1$ Hz, 2H), 7.26 – 7.22 (m, 2H), 4.73 (d, $J = 6.5$ Hz, 2H), 2.35 – 2.23 (m, 1H), 1.49 – 1.19 (m, 16H), 0.95 – 0.78 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.31 (dd, $J = 252.9, 19.6$ Hz), 137.95 – 137.55 (m), 132.43 (s), 130.18 (s), 128.01 (s), 127.45 (s), 110.44 – 109.75 (m), 60.14 (s), 39.24 (s), 31.96 (s), 31.61 (s), 31.34 (s), 29.69 (s), 28.65 (s), 26.39 (s), 23.09 (s), 22.79 (s), 14.21 (s, 2C); ^{19}F NMR (377 MHz, CDCl_3) δ -134.09; MS(EI): $m/z = 487$ [M^+].

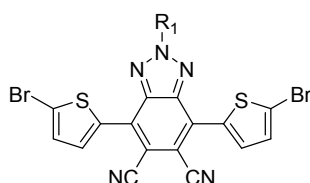
2-(2-butyloctyl)-4,7-di(thiophen-2-yl)-2H-benzotriazole-5,6-dicarbonitrile (dTdCNBTz)



A degassed solution of **2** (0.875 g, 1.79 mmol), KCN (0.6 g, 9.23 mmol) and 18-crown-6 (0.243 g, 0.923 mmol) in THF (15 mL) was heated in a sealed pressure tube (20 mL microwave vial) at 80 $^{\circ}\text{C}$ for

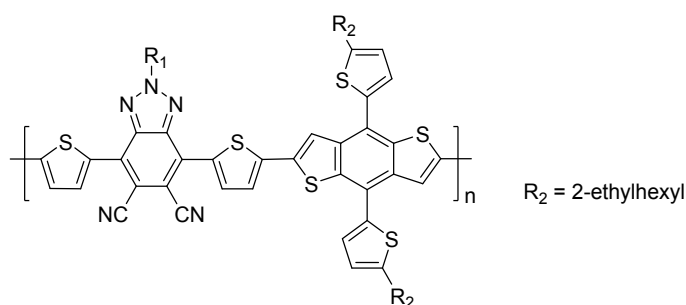
16 h. The reaction was heated to reflux for 16 h. The cooled reaction mixture was diluted with CH₂Cl₂ (100 mL) and extracted thoroughly with water (5 x 50 mL). The aqueous extracts were separated from the organic layer and treated with ammonia solution (28%) to destroy any residual cyanide present. The organic extracts were dried (MgSO₄), filtered and concentrated under reduced pressure. The crude product was then purified using column chromatography using ethyl acetate/hexane (1:9, v:v) to afford **dTdCNBTz** (510 mg, 1.02 mmol). Yield: 57%; Mpt. 68°C; ¹H NMR (400 MHz, CDCl₃) δ 8.24 (dd, *J* = 3.9, 1.1 Hz, 2H), 7.70 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.29 (dd, *J* = 5.1, 3.9 Hz, 2H), 4.78 (d, *J* = 6.5 Hz, 2H), 2.33 – 2.22 (m, 1H), 1.46 – 1.19 (m, 16H), 0.93 – 0.81 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 142.99, 133.39, 131.92, 131.23, 131.09, 128.01, 117.03, 108.02, 61.09, 39.35, 31.89, 31.51, 31.24, 29.61, 28.53, 26.29, 23.01, 22.75, 14.21, 14.15; MS(EI): *m/z* = 501 [M⁺].

4,7-bis(5-bromothiophen-2-yl)-2-(2-butyloctyl)-2H-benzotriazole-5,6-dicarbonitrile (*bis-Br(dTdCNBTz)*)



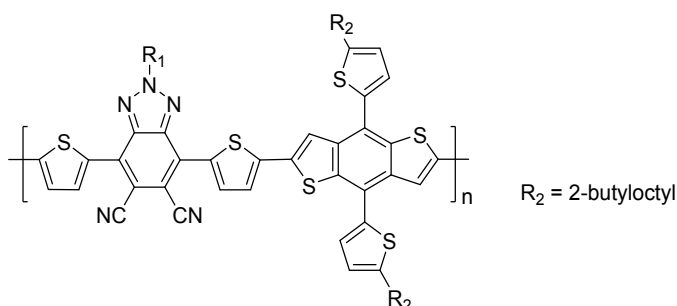
To a solution of **dTdCNBTz** (410 mg, 0.817 mmol) in chloroform (20 mL) was added bromine (0.300 g, 1.88 mmol) and the reaction stirred in the absence of light for 24 h. The reaction was monitored by TLC and ¹H NMR and another 1 equivalent of bromine (0.131 mg, 0.817 mmol) was added in small portions over 6 h until completion. The reaction mixture was quenched into a saturated solution of sodium sulfite and extracted with CH₂Cl₂ (3 x 20 mL). The organics were combined, dried (MgSO₄), filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography over silica using CH₂Cl₂/hexane (1:1, v:v) to afford the **bis-Br(dTdCNBTz)** as a yellow solid (310 mg, 0.470 mmol). Yield: 57.5%; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 4.1 Hz, 2H), 7.24 (d, *J* = 4.1 Hz, 2H), 4.79 (d, *J* = 6.3 Hz, 2H), 2.33 – 2.20 (m, 1H), 1.49 – 1.20 (m, 16H), 0.95 – 0.82 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 142.51, 134.83, 132.15, 130.98, 129.91, 119.78, 116.76, 107.56, 61.07, 39.47, 31.94, 31.53, 31.29, 29.68, 28.58, 26.30, 23.08, 22.79, 14.22 (2C); EI-HRMS (*m/z*): Calculated for C₂₈H₂₈N₅S₂Br₂ [M-H]⁺: 656.0153, found 656.0133.

P1



Bis-Br(dTdCNBTz) (200 mg, 0.303 mmol), **BDT(T-EH)** (274 mg, 0.303 mmol), $\text{Pd}_2(\text{dba})_3$ (5.5 mg, 0.006 mmol), $\text{P}(\text{o-tol})_3$ (7.4 mg, 0.024 mmol) and a stirrer bar were added to a 5 mL high pressure microwave reactor vial. The vial was sealed with a septum and flushed with argon, before degassed *o*-xylene (2 mL) was added. The whole solution was then degassed for 20 min under argon and the argon inlet removed. The vial was heated by microwave irradiation to 100 °C for 2 min, 140 °C for 2 min, 160 °C for 2 min, 180 °C for 10 min and 200 °C for 25 min. The polymer was cooled to RT and precipitated in methanol (100 mL), stirred for 30 min and filtered through a Soxhlet thimble. The polymer was extracted using Soxhlet apparatus (methanol, acetone, hexane, chloroform, chlorobenzene) under argon. The polymer remaining in the thimble was dissolved in hot TCB and precipitated in methanol (200 mL) to yield a dark blue polymer **P1**. Chloroform fraction: 12 mg, chlorobenzene fraction: 10 mg. Chloroform fraction: $^1\text{H NMR}$ (400 MHz, TCE-d_2 , 130°C) δ 8.45 – 8.23 (m, 2H), 7.95 – 7.61 (m, 2H), 7.60 – 7.28 (m, 4H), 7.15 – 6.95 (m, 2H), 5.00 – 4.80 (br, 2H), 3.21 – 2.93 (m, 4H), 2.51 – 2.32 (br, 1H), 2.01 – 1.73 (br, 3H), 1.74 – 1.27 (m, 31H), 1.26 – 0.89 (m, 18H).

P2



The same polymerisation conditions were used as above. **Bis-Br(dTdCNBTz)** (100.2 mg, 0.152 mmol), **BDT(T-BO)** (154.1 mg, 0.152 mmol), $\text{Pd}_2(\text{dba})_3$ (2.86 mg, 0.003 mmol), $\text{P}(\text{o-tol})_3$ (3.77 mg, 0.012 mmol). Yield: 91% (164 mg, 0.138 mmol); Chloroform fraction: 76 mg M_n : 26.0 kDa, M_w : 87.51 kDa, M_w/M_n (\bar{D}): 3.37. Chlorobenzene fraction: 88 mg M_n : 78.2 kDa, M_w : 114.3 kDa, M_w/M_n (\bar{D}): 1.46; $^1\text{H NMR}$ (400 MHz, TCE-d_2 , 130°C) δ 8.47 – 8.30 (m, 2H), 7.93 – 7.69 (m, 2H), 7.65 – 7.33 (m, 4H), 7.18 – 7.00 (m, 2H), 4.98 – 4.77 (m, 2H), 3.21 – 2.93 (m, 4H), 2.53 – 2.33 (m, 1H), 2.04 – 1.81 (m, 3H), 1.72 – 1.27 (m, 47H), 1.16 – 0.85 (m, 18H); Anal. Calcd. for $\text{C}_{70}\text{H}_{85}\text{N}_5\text{S}_6$ C 70.72, H 7.21, N 5.89; found: C 70.62, H 7.11, N 5.84.

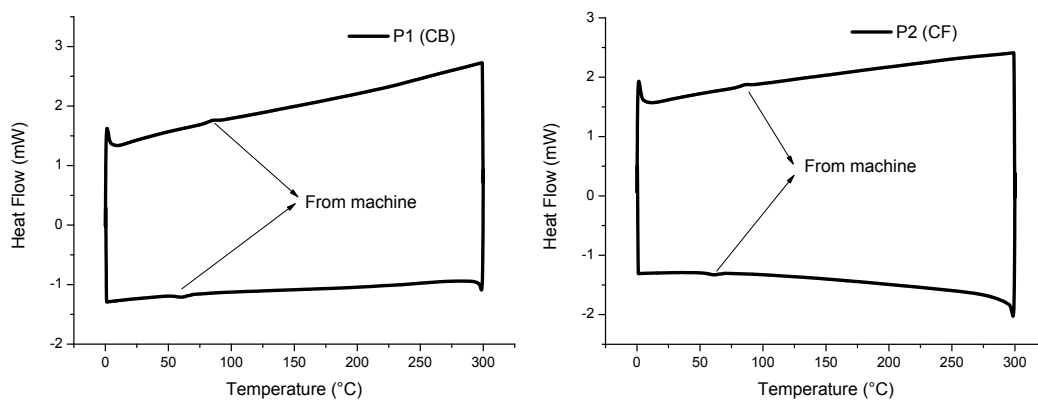


Figure S1: DSC traces (endo up) recorded at a heating and cooling rate of $10^{\circ}\text{C}/\text{min}$ under nitrogen (second heating/cooling cycle)

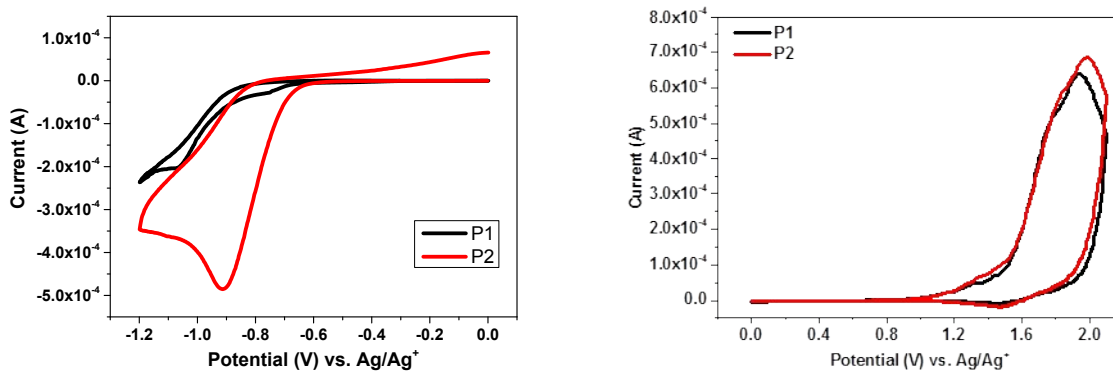


Figure S2: Cyclic voltammograms for **P1** and **P2** scanning over negative (left) and positive (right) potentials. Measurements were taken in acetonitrile/ $[\text{n-Bu}_4\text{N}]\text{PF}_6$ solutions (0.1M). Scan rate: 0.1 Vs^{-1} .

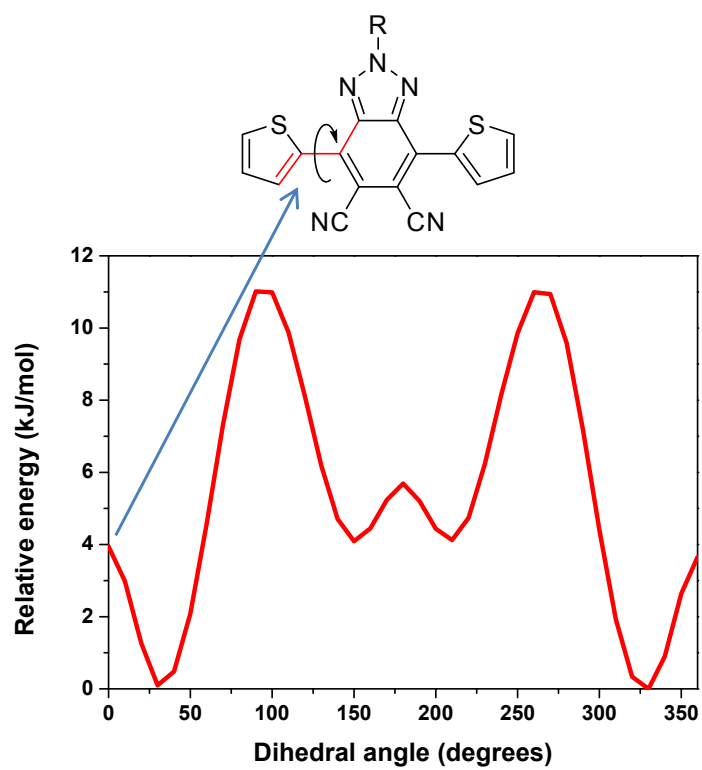


Figure S3: Potential energy scans of the T-dCNBT bond of the monomer from 0° to 360° calculated using DFT (B3LYP, 6-311G(d)).

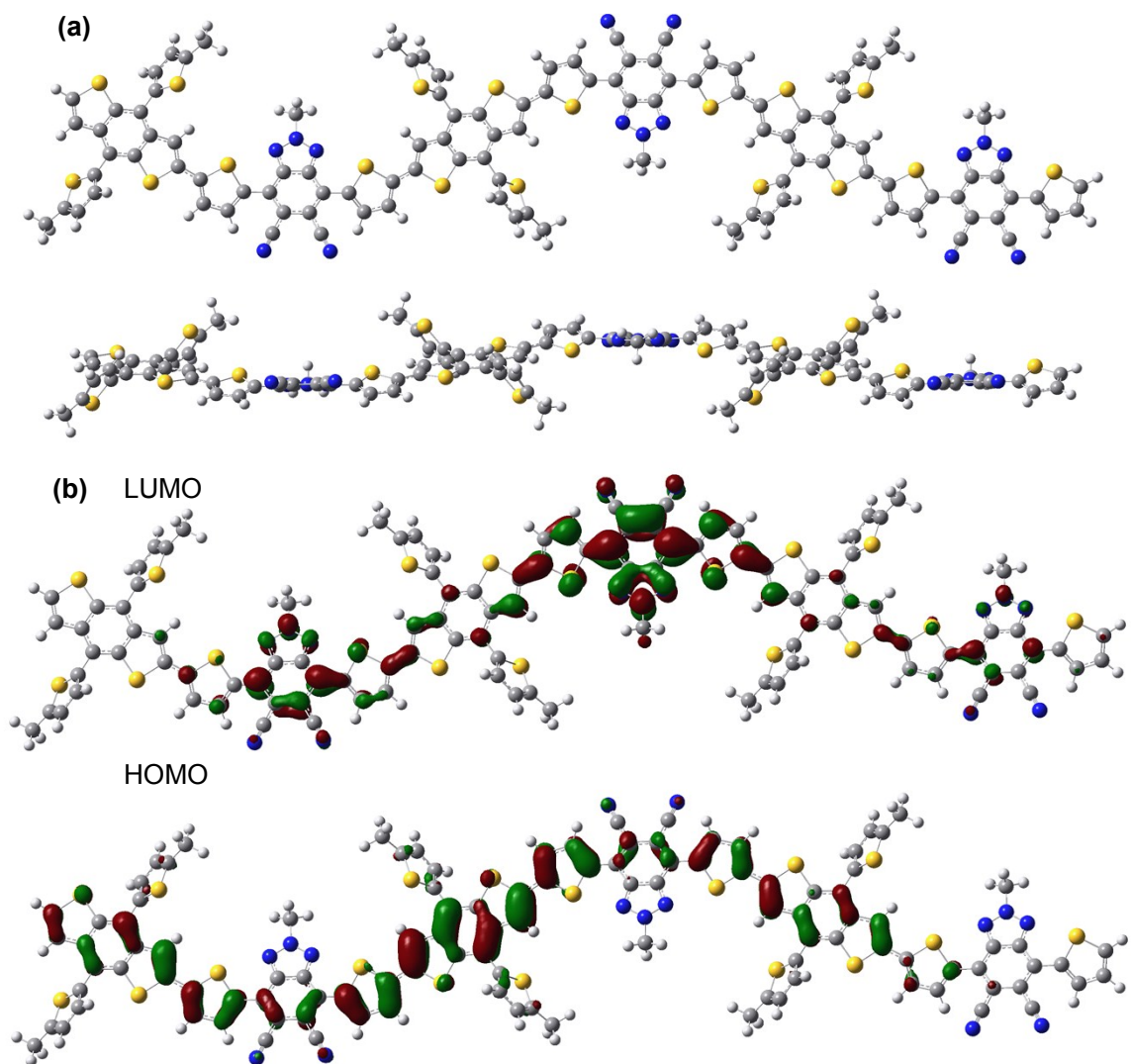


Figure S4: a) Molecular geometry and (b) frontier molecular orbitals of PDCBTzBDT polymers as calculated using Gaussian 09 at the B3LYP level of theory with the 6-311G(d,p) basis set. The T-BTz-T geometry is based on the preferred energy scan.

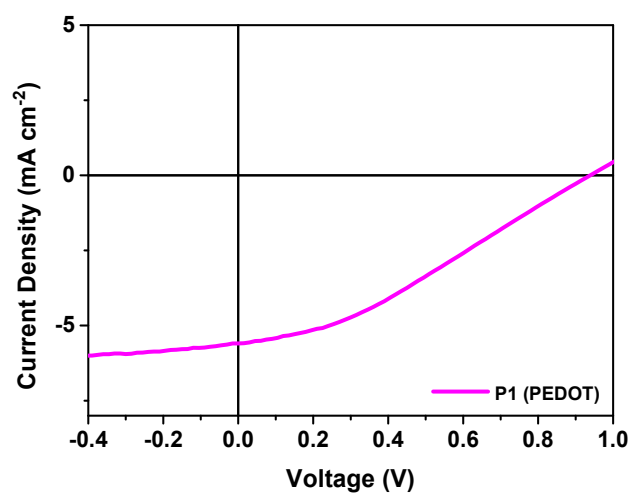


Figure S5: J-V curve for P1 using PEDOT:PSS as the hole transporting layer

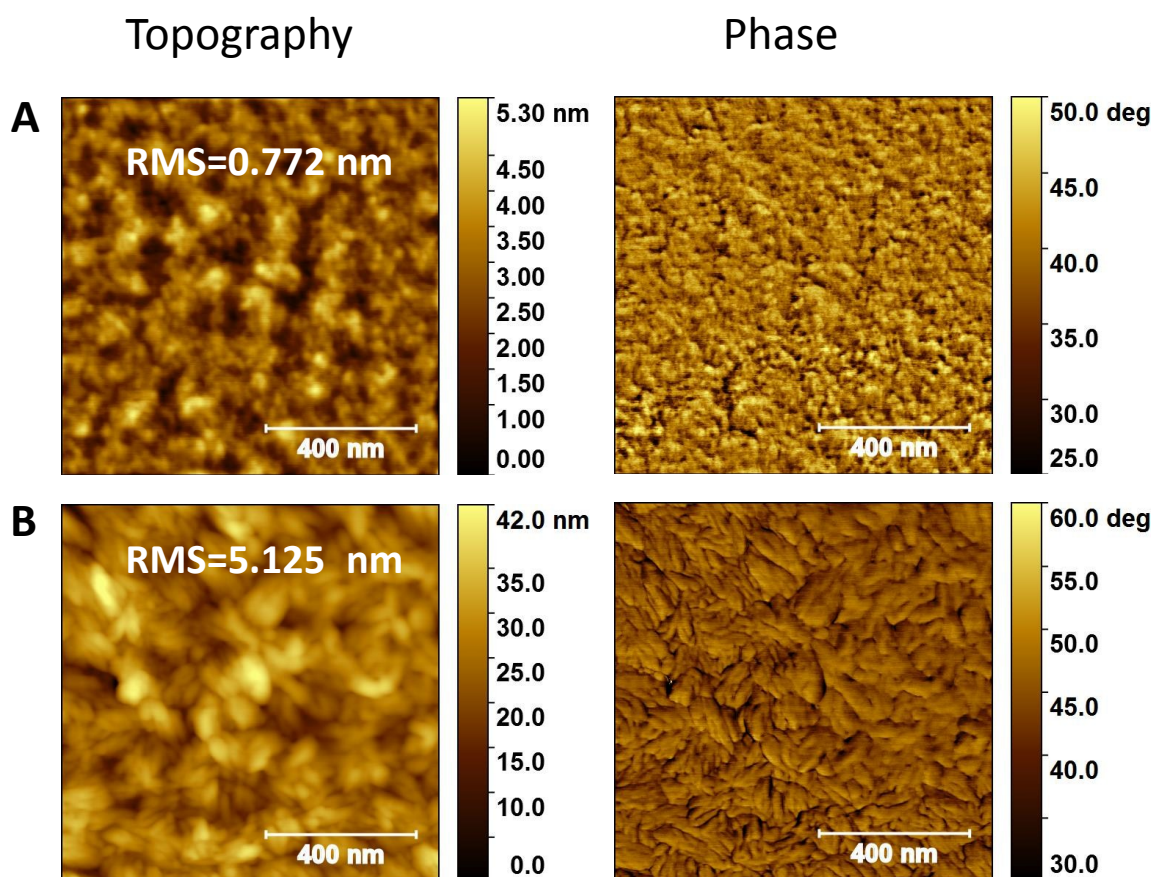


Figure S6: AFM topography (left) and phase (right) images of A) PEDOT:PSS on ITO coated glass and B) CuSCN on ITO coated glass

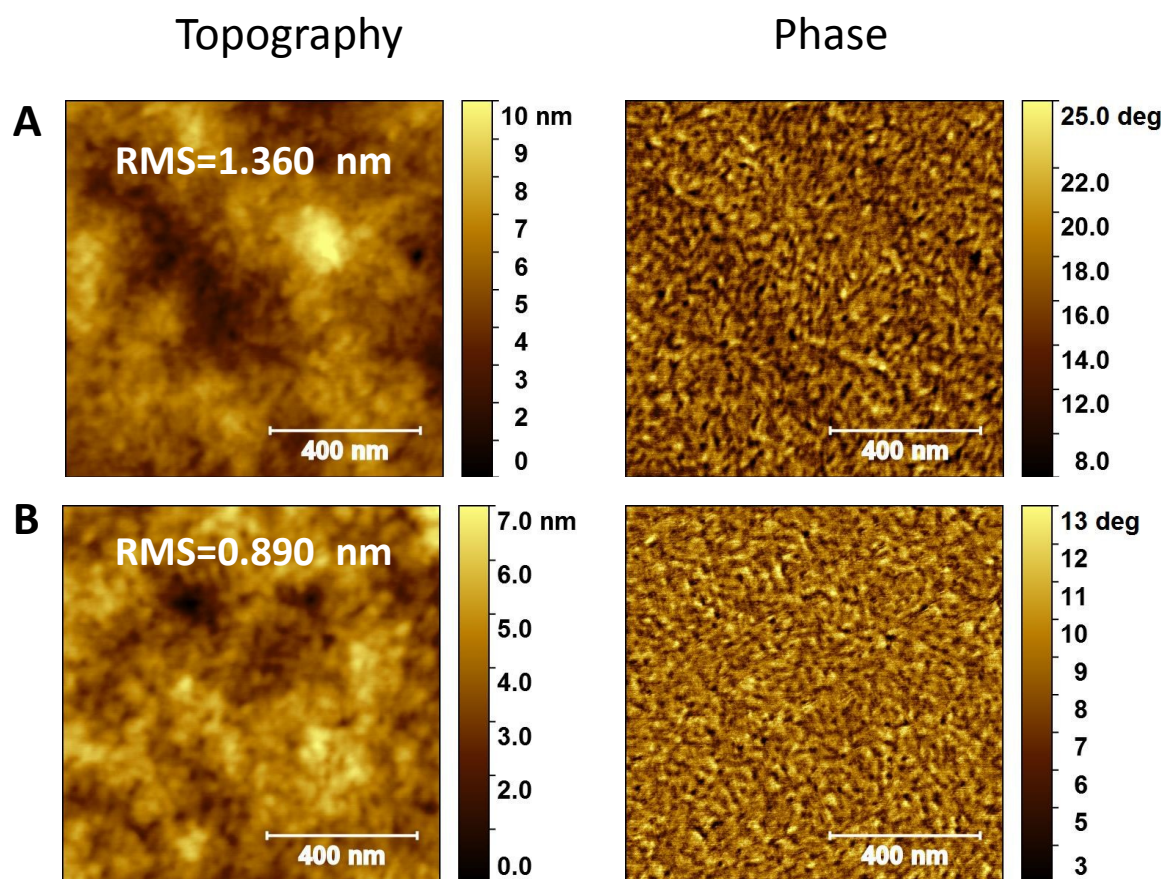


Figure S7: AFM topography (left) and phase (right) images of A) Chlorobenzene fraction of **P2** coated onto CuSCN layer and B) chlorobenzene fraction of **P2** coated onto PEDOT:PSS layer.

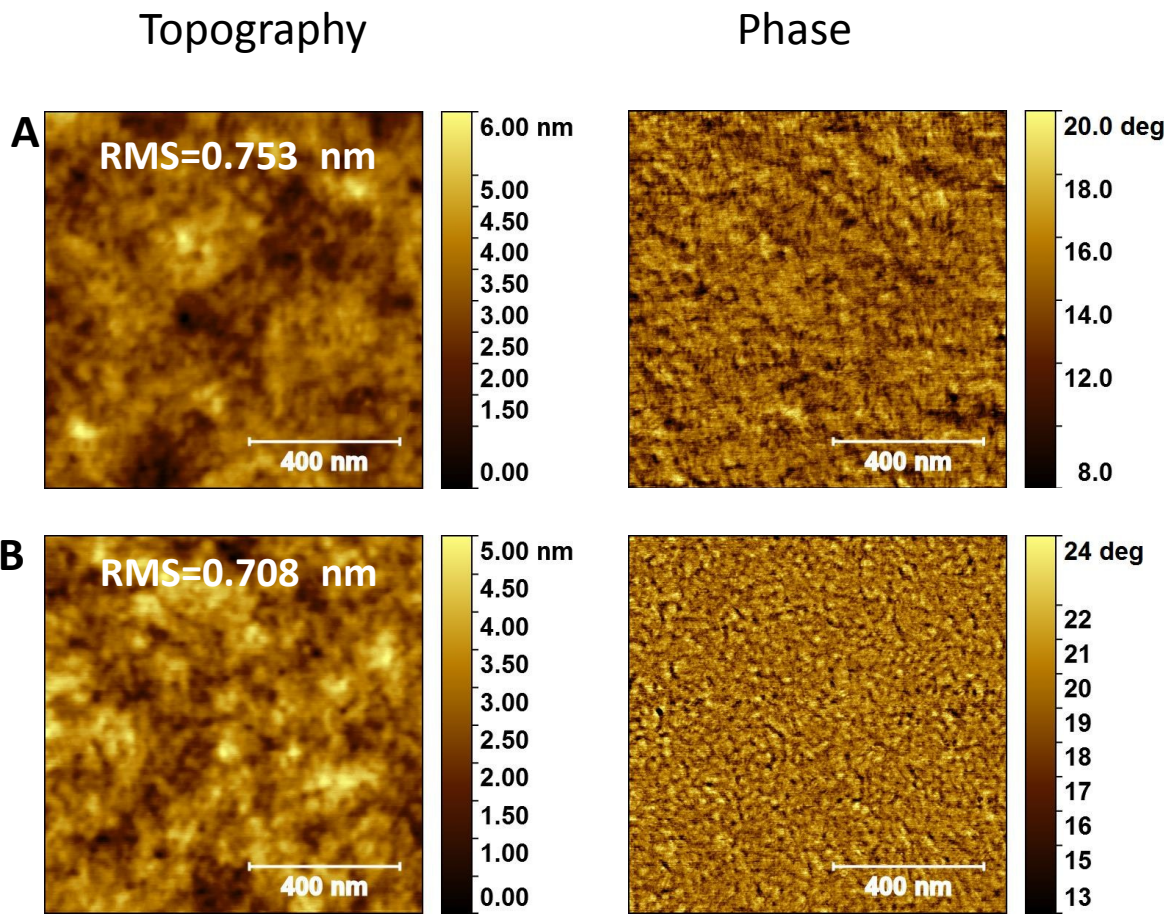


Figure S8: AFM topography (left) and phase (right) images of A) Chloroform fraction of **P2** coated onto CuSCN layer and B) chloroform fraction of **P2** coated onto PEDOT:PSS layer.

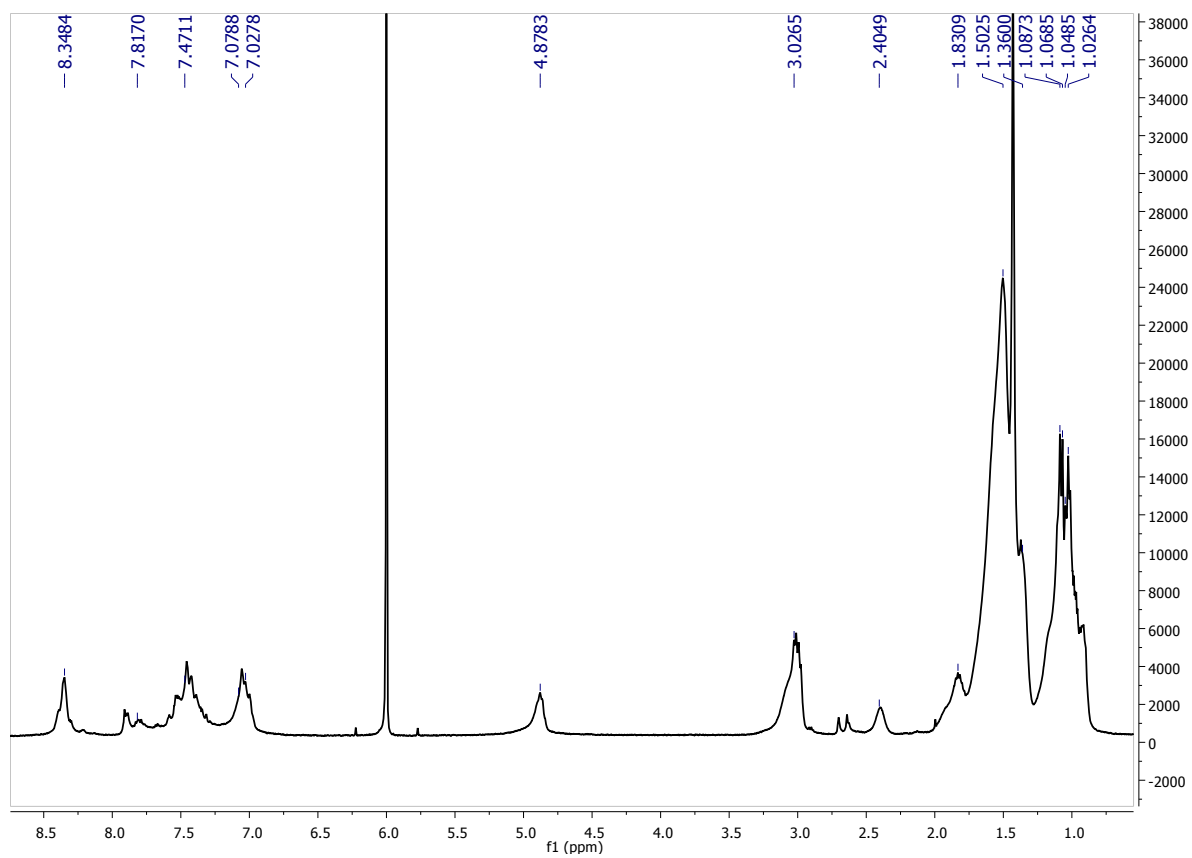


Figure S9: ^1H NMR of P1.

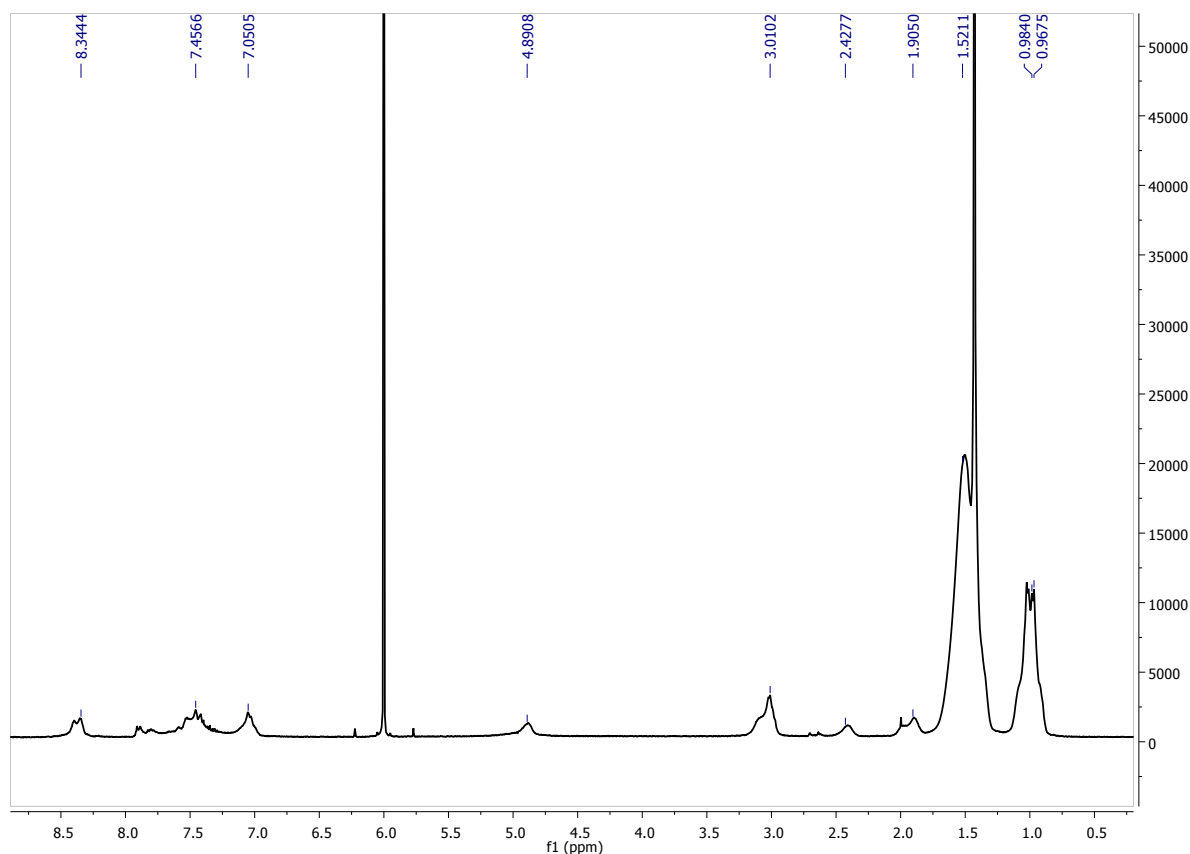


Figure S10: ¹H NMR of P2.

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian09, Revision C.01. Wallingford, CT 2009.