Supporting Information

Phthalimide-Based Polymers for High Performance Organic Thin-Film Transistors

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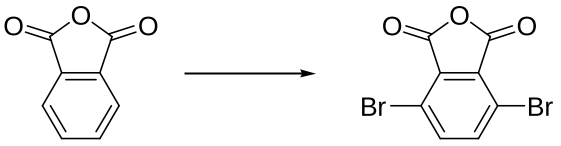
Materials and Methods. THF, acetonitrile and toluene were distilled from appropriate drying agents and stored over molecular sieves under argon. rr-P3HT was purchased from American Dye Source, Inc. 5,5′-bis(tributylstannyl)-3,3′-bis(dodecyloxy)-2,2′-bithiophene (**3**) was synthesized via published procedures.[1] All other reagents were used as received except where noted. Unless otherwise stated, all manipulations and reactions were carried out under argon atmosphere using standard Schlenk techniques. ^{1}H and ^{13}C spectra were recorded on a Varian INOVA 400MHz spectrometer (purchased under the CRIF Program of the National Science Foundation, grant CHE-9974810). Chemical shifts were referenced to residual protio-solvent signals. GC-MS data were collected from an Agilent technologies 6890N GC with 5973 MSD. Relative molecular weights of polymers were measured using a Waters 600E HPLC system, driven by Waters Empower Software and equipped with two linear mixed-bed GPC columns (American Polymer Standards Corporation, AM Gel Linear/15) in series. Eluting polymers were detected with both refractive index and photodiode array detectors and the system was calibrated with 11 narrow PDI polystyrene samples in the range 580 to 2 x10^6 Da with THF at a flow rate of 1mL/min. Melting points are reported as the endothermic maxima of 1st order transitions detected by differential scanning calorimetry (Mettler 822^e, heating rate = 10 º C/min, nitrogen purge). TGA curves were recorded on a TA Instrument (Model No. TGA Q500). UV-Vis data were recorded on a Varian Cary 1 UV-Visible spectrophotometer. Elemental analysis and ICP were performed by Robertson Microlit Laboratories. Cyclic voltammetry measurements of polymers were carried out under nitrogen atmosphere using a BAS-CV-50W voltammetric analyzer with 0.1 M tetra-*n*-butylammonium hexafluorophosphate in actonitrile as supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode and silver wire reference electrode were employed and Fc/Fc^+ was used as reference for all measurements. The scan rate was 50 mV/S. Polymer films were produced by drop casting from 0.2 % (w/w) toluene solutions. The supporting electrolyte solution was thoroughly purged with N_2 before all CV measurements. WAXD data of polymers were collected on Bruker-Nonius X8 Proteum (purchased under NSF MRI program grant number 0319176) using an area detector and extruded, oriented fibers mounted perpendicular to the incoming beam.



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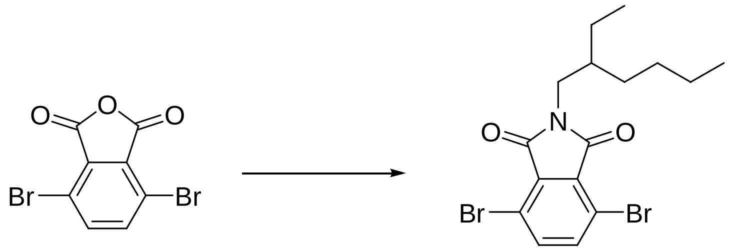
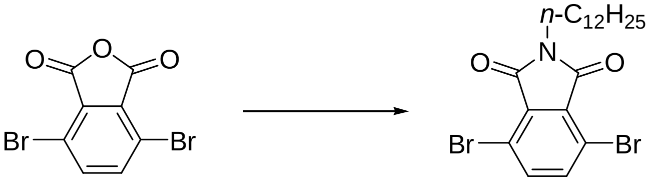
3,6-dibromophthalic anhydride[2] (2). A mixture of phthalic anhydride (80 g, 0.54 mol), oleum (30 % free SO_3, 125 ml), bromine (104 g, 0.65 mol), and iodine (0.51 g, 2 mmol) was stirred at 60 °C for 24 hours. After cooling to room temperature, dichloromethane was added to the reaction mixture and the whole was carefully diluted with D.I. H_2O. The whole was filtered and the organic layer was concentrated via rotary evaporation to a brown solid. This brown solid was recrystallized twice from acetic acid to provide colorless crystals (36 g, 22 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.81 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 159.15, 141.58, 131.15, 120.14. mp: 213 °C. GC-MS: m/z: 304 ($C_8H_2Br_2O_3^+$), 262 (100%).



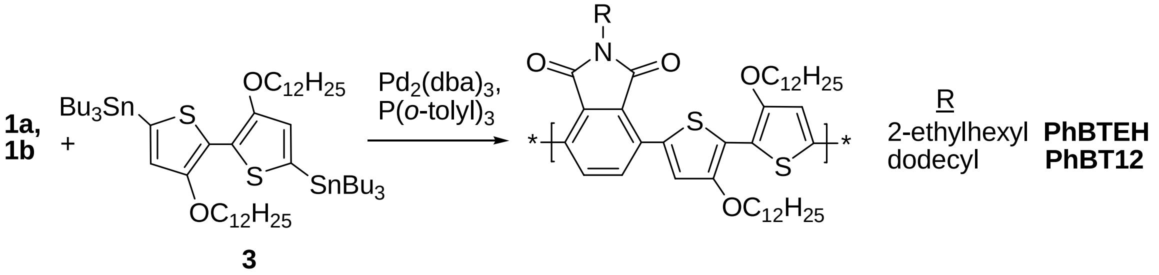
1a

N-(2-ethylhexyl)-3,6-dibromophthalimide (1a). 3,6-dibromo phthalic anhydride (1.53 g, 5 mmol), 2-ethylhexyl amine (0.84 g, 6.5 mmol) and glacial acetic acid (30 ml) were combined and refluxed under argon for two hours. After most of the acetic acid was removed under reduced pressure, target **1a** was separated via column chromatography (silica gel, dichloromethane:hexanes 1:3). Colorless crystals were obtained after recrystallization from hexanes (1.88 g, 90 %). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.63 (s, 2H), 3.56 (d, 2H), 1.80 (m, 1H), 1.29 (m, 8H), 0.88 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.34, 139.71, 131.42, 117.71, 42.66, 38.46, 30.77, 28.76, 24.09, 23.16, 14.26, 10.59. mp: 65 °C. GC-MS: m/z: 415 ($C_{16}H_{19}Br_2NO_2^+$), 319 (100%). Anal. Calcd for $C_{16}H_{19}Br_2NO_2$(%): C, 46.07; H, 4.59; N,3.36. Found (%): C, 46.09; H, 4.32; N, 3.37.



1b

N-dodecyl-3,6-dibromophthalimide (1b). Compound **1b** was prepared and isolated as above for compound **1a** in 94 % isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.62 (s, 2H), 3.66 (t, 2H), 1.65 (m, 2H), 1.27 (m, 18H), 0.85 (t, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.05, 139.68, 131.51, 117.69, 38.89, 32.13, 29.83, 29.78, 29.65, 29.55, 29.35, 28.53, 27.04, 22.90, 14.34 (**Note:** two peaks in ^{13}C NMR spectrum overlap). mp: 85 °C. GC-MS: m/z: 471 ($C_{20}H_{27}Br_2NO_2^+$), 318 (100%). Anal. Calcd for $C_{20}H_{27}Br_2NO_2$(%): C, 50.76; H, 5.75; N,2.96. Found (%): C, 50.77; H, 5.47; N, 3.05.



Polymer **PhBTEH.** In an air-free flask, monomers **1a** (83.43 mg, 0.2 mmol) and **3** (222.60 mg, 0.2 mmol) were combined under argon followed by addition of a mixture of tris(dibenzylideneacetone) dipalladium (0) and tri(*o*-tolyl)phosphine (1:8 molar ratio between $Pd_2(dba)_3$ and P(*o*-tolyl)$_3$; Pd loading: 0.03 equiv). The flask and its contents were subjected to 3 pump/purge cycles with argon followed by addition of anhydrous, degassed THF (4 ml) via syringe. The sealed reaction mixture was stirred at 80 ºC for 24 hours. After cooling to room temperature, the deeply colored reaction mixture was dripped into 100 ml vigorously stirred methanol (containing 5 ml 12 M HCl). The precipitated solid was stirred for 4 hours and collected by centrifugation and decantation. The solid polymer was dissolved in chloroform and reprecipitated into methanol. After filtration and drying under reduced pressure, the polymer was subjected to sequential Soxhlet extraction using methanol, acetone and hexane (24 hours for each solvent) and finally chloroform. The chloroform solution was concentrated to 20 ml, dripped into vigorously stirred methanol and the resulting solid collected by centrifugation and decantation. After drying in vacuo, a blue solid with copper-like metallic luster was obtained (151.72 mg, 96 %). ^{1}H NMR ($C_2D_2Cl_4$, 100 ºC, 400 MHz, ppm): δ 7.94 (brs, 2H), 7.90 (brs, 2H), 4.35 (brs, 4H), 3.69 (brs, 2H), 2.04 (m, 4H), 1.97 (m, 1H), 1.69 (brs, 4H), 1.38 (m, 40H), 0.99 (m, 12H). Anal. Calcd for $C_{48}H_{71}NO_4S_2$(%): C, 72.96; H, 9.06; N,1.77. Found (%): C, 72.69; H, 8.81; N, 1.79. ICP analysis revealed a Pd content of 286 ppm.

Polymer **PhBT12**. **PhBT12** was prepared and isolated in a manner similar to that employed for **PhBTEH**. After drying in vacuo, a blue solid with copper-like metallic luster was obtained (90 %). ^{1}H NMR ($C_2D_2Cl_4$, 100 ºC, 400 MHz, ppm): δ 7.96 (brs, 2H), 7.89 (brs, 2H), 4.35 (brs, 4H), 3.76 (brs, 2H), 2.04 (brs, 4H), 1.79 (brs, 2H), 1.69 (brs, 4H), 1.39 (m, 50H), 0.93 (m, 9H). Anal. Calcd for $C_{52}H_{79}NO_4S_2$ (%): C, 73.80; H, 9.41; N, 1.66. Found (%): C, 73.55; H, 9.36; N, 1.63. ICP analysis revealed a Pd content of 839 ppm.

Fabrication and characterization of thin-film transistors

Organic thin-film transistors (OTFTs) were fabricated in bottom-contact, bottom-gate geometry.[3, 4, 5] Heavily n-doped silicon with thermally grown silicon dioxide (300 nm thick, C_0 = 11 nF/cm^2) served as gate electrode with gate dielectric. Source and drain electrodes were patterned with 2 nm thick chromium adhesive layer and 60 nm of gold by using serial processes of photolithography, metal deposition, and lift-off. The transistor channel of each device has width (W) of 800 μm and length (L) of 20 μm. Before polymer deposition, the silicon dioxide surface was treated with octyltrichlorosilane (OTS-8) via vapor deposition. Substrates and a few drops of OTS-8 were placed in a vacuum desiccator at 60 °C for more than 4 h. Then the substrates were heated at 120 °C for 20 minutes. Polymer solution (4 – 6 mg/mL) in 1,2-dichlorobenzene was spin–coated onto substrates at 1000 rpm for 90 s to form thin films (30 – 60 nm). The films were dried under reduced pressure at 60 °C overnight prior to device characterization. Electrical characteristics of these OTFTs were measured using a Keithley 4200 semiconductor characterization system. All fabrication and characterization was carried out in ambient air under light except vacuum deposition and drying. The mobility was calculated from the saturation region ($-V_{ds} > -(V_g-V_t)$) of transfer curves (I_{ds} vs. V_g) at source-drain voltage (V_{ds}) of -60 V or -80 V with following equation:

$$I_{ds} = (W/2L)\mu C_0 (V_g - V_t)^2$$

Average device characteristics were calculated for **PhBTEH** and **PhBT12** from 36 and 32 devices, respectively.

Surface morphology of polymer thin-films was imaged directly from transistors by using Veeco Dimension 3100 scanning probe microscope in standard tapping mode. Polymer thin films for X-Ray Diffraction (XRD) were prepared by drop-casting on microscope slide glass. Before film deposition, the glass surfaces were cleaned and modified with OTS-8 as described above. After polymer deposition, samples were dried under vacuum at 60 °C overnight. Diffraction data was collected from a Bruker-AXS D8 Focus diffractometer in θ-2θ scans (0.01 ° step size, 3 s exposures/step). The diffracted beam (Cu Kα, 40 kV, 40 mA) was passed through 2.0 mm anti-scattering slit, nickel filter, and 1.0 mm detector slit.

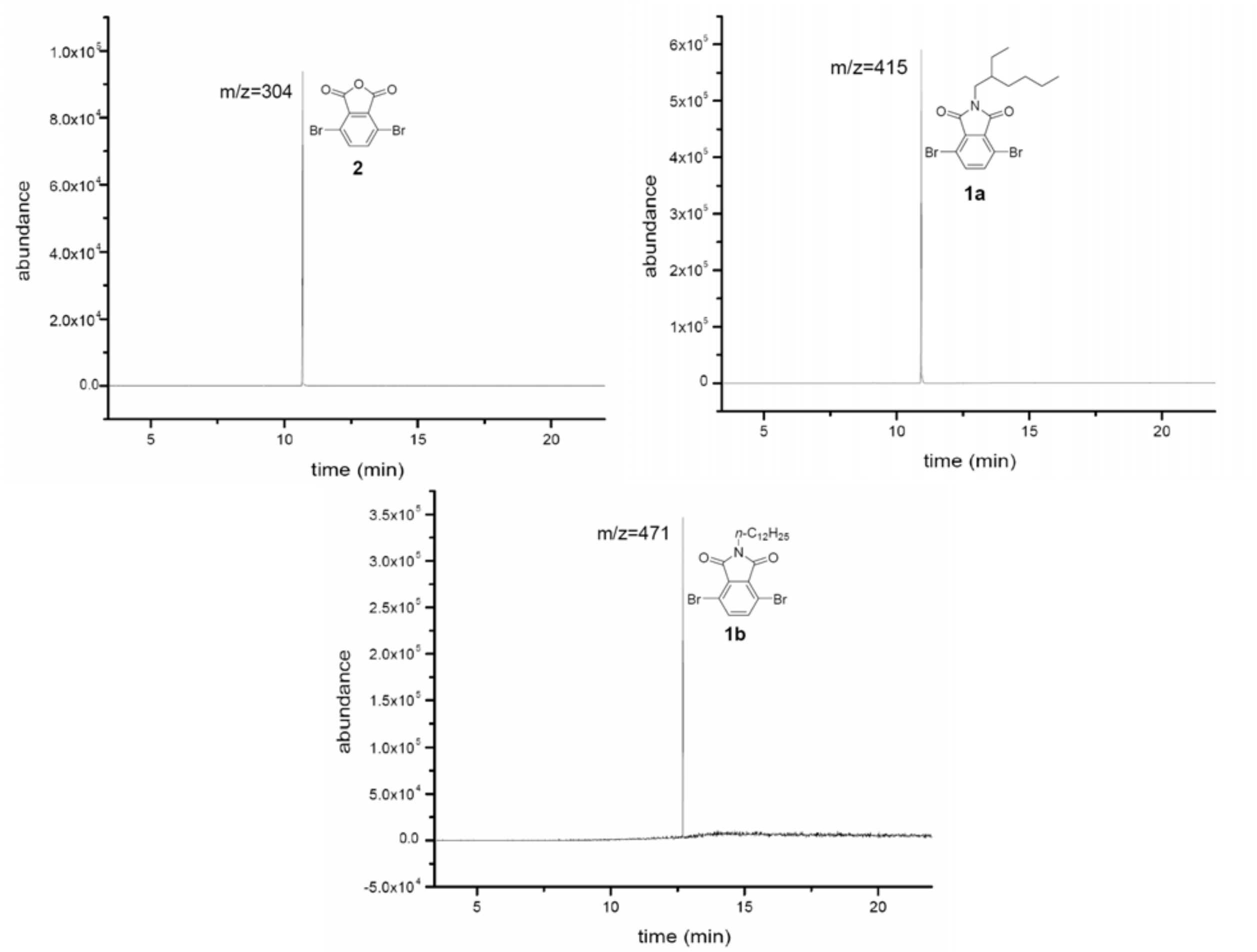


Figure S1 . GC chromatograms (total ion count) from GC-MS measurements.

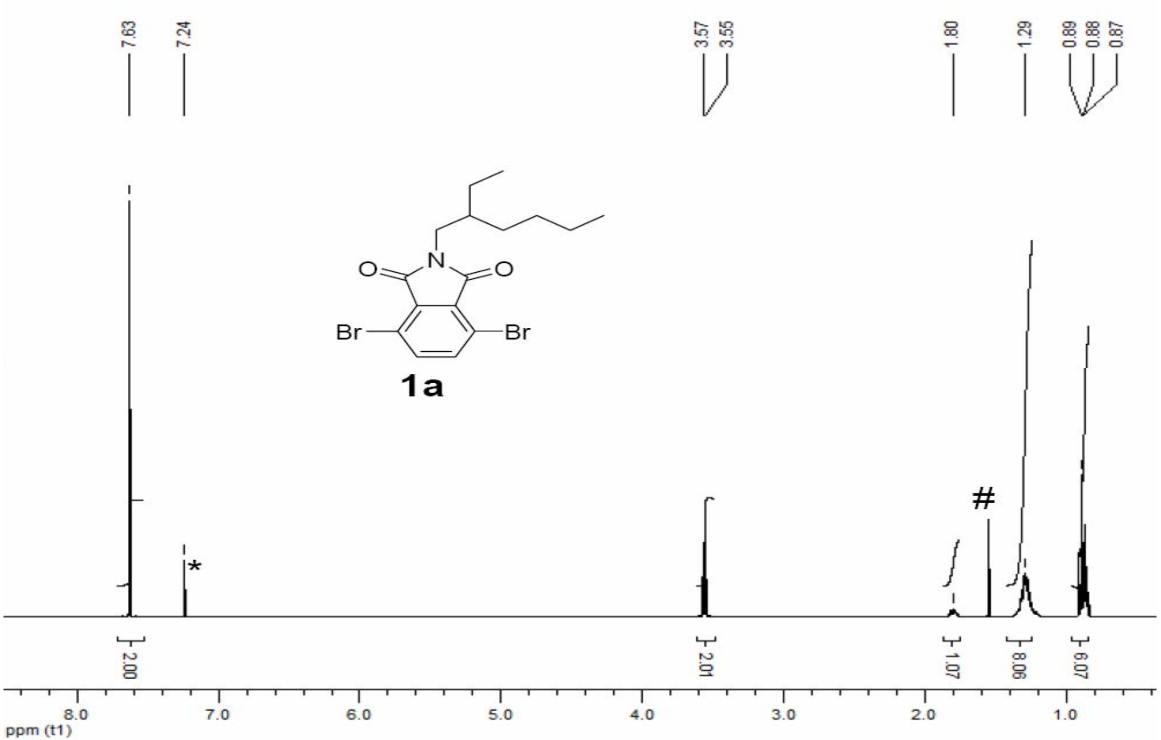


Figure S2. ^{1}H NMR spectrum of **1a** (r.t., in $CDCl_3$, *: solvent, #: H_2O)

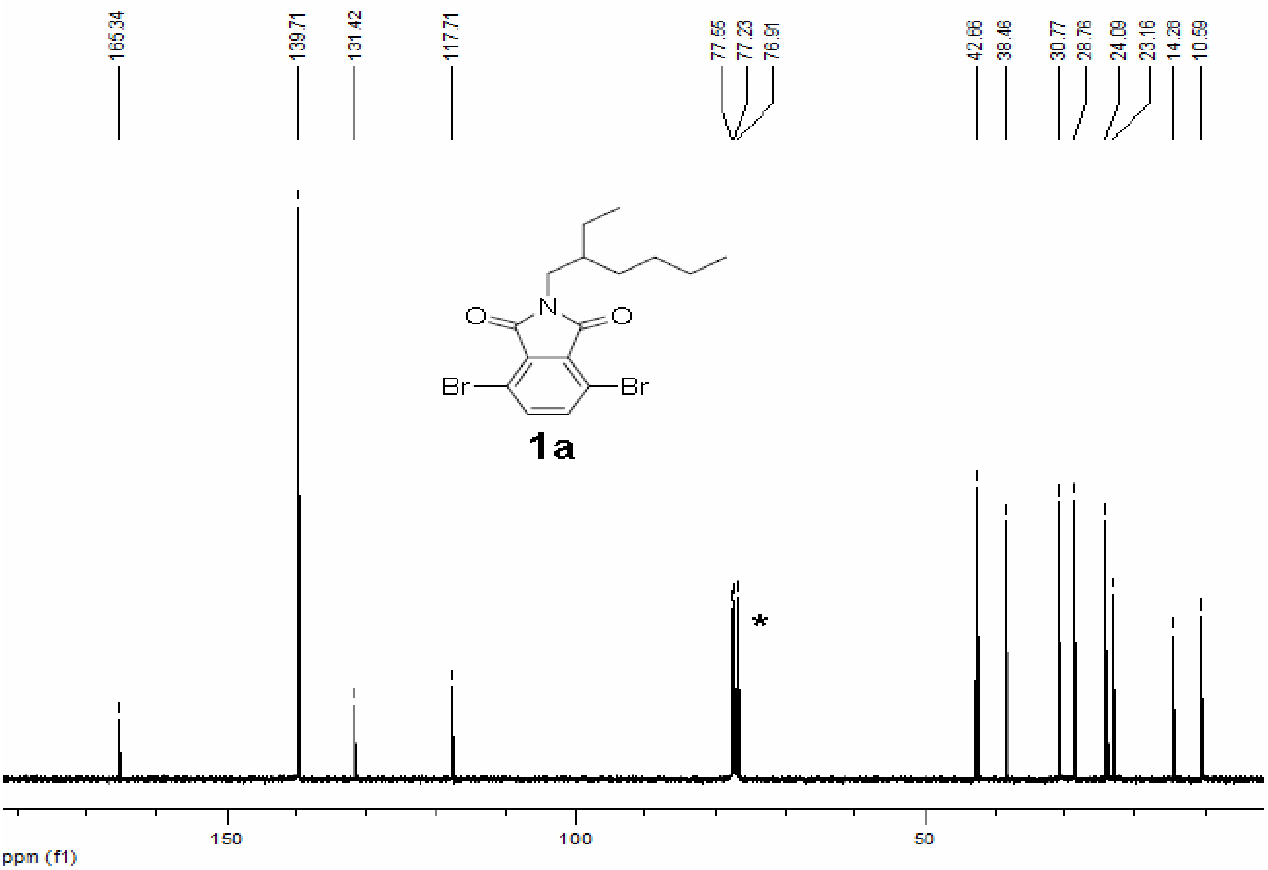


Figure S3. ^{13}C NMR spectrum of **1a** (r.t., in $CDCl_3$, *: solvent)

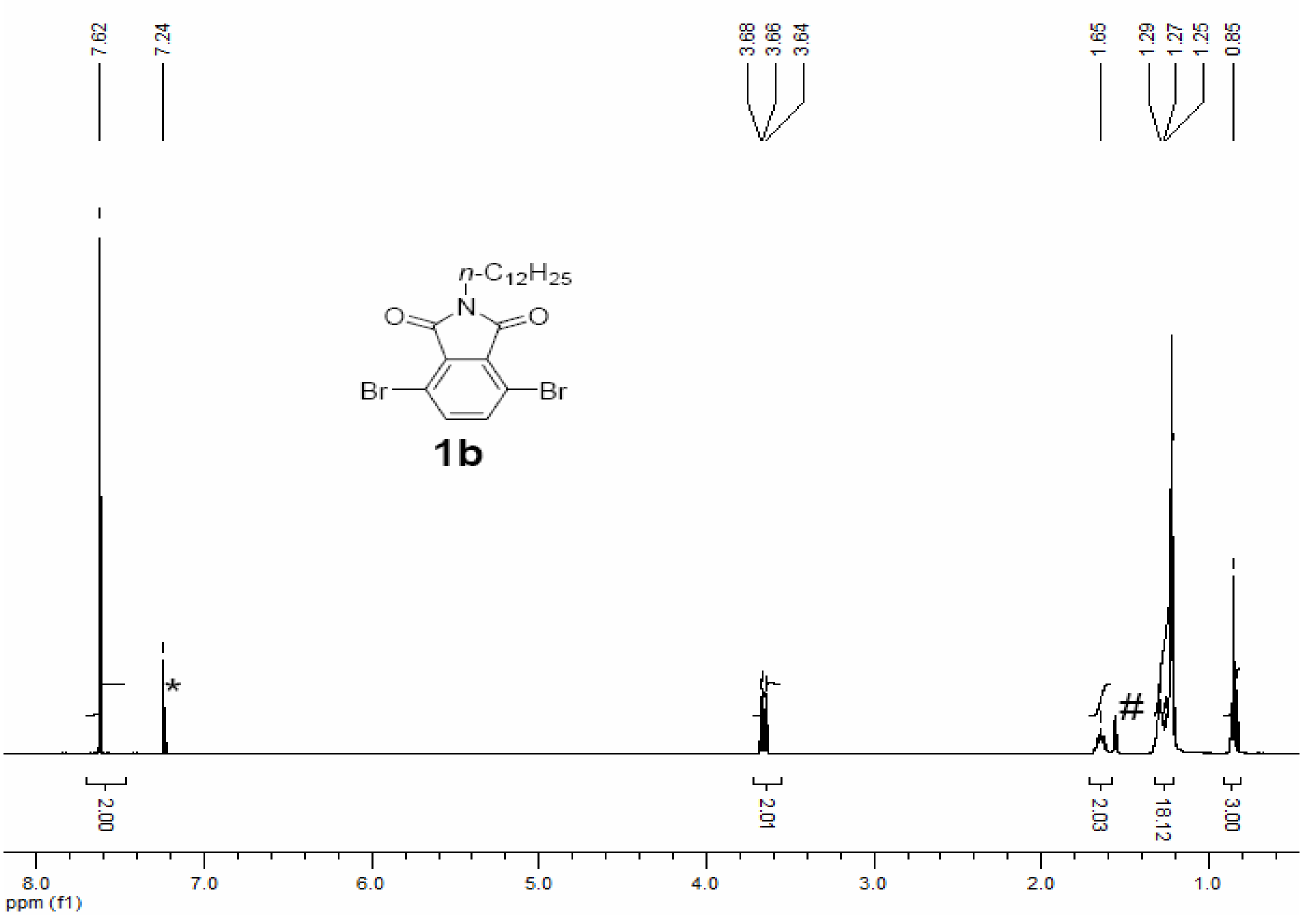


Figure S4. ^{1}H NMR spectrum of **1b** (r.t., in $CDCl_3$, *: solvent, #: H_2O)

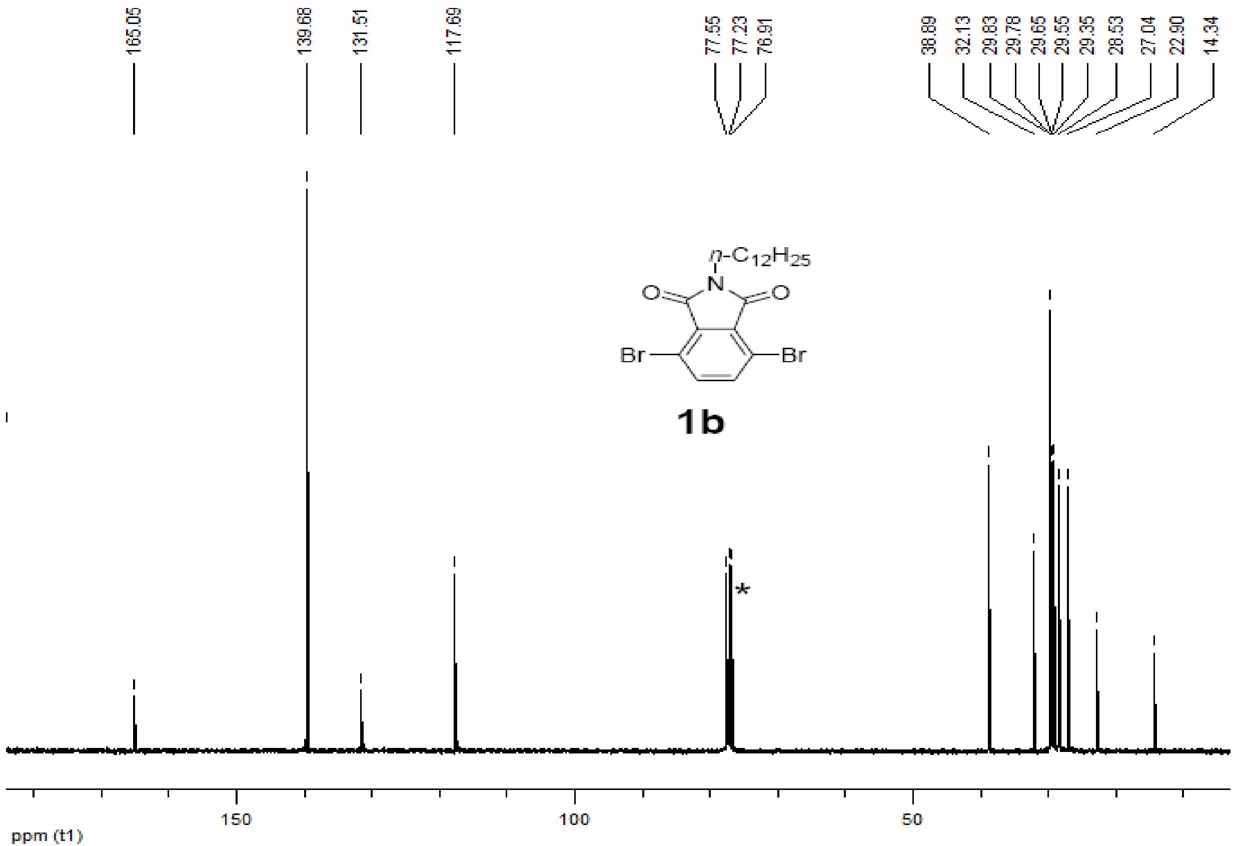


Figure S5. ^{13}C NMR spectrum of **1b** (r.t., in $CDCl_3$, *: solvent)

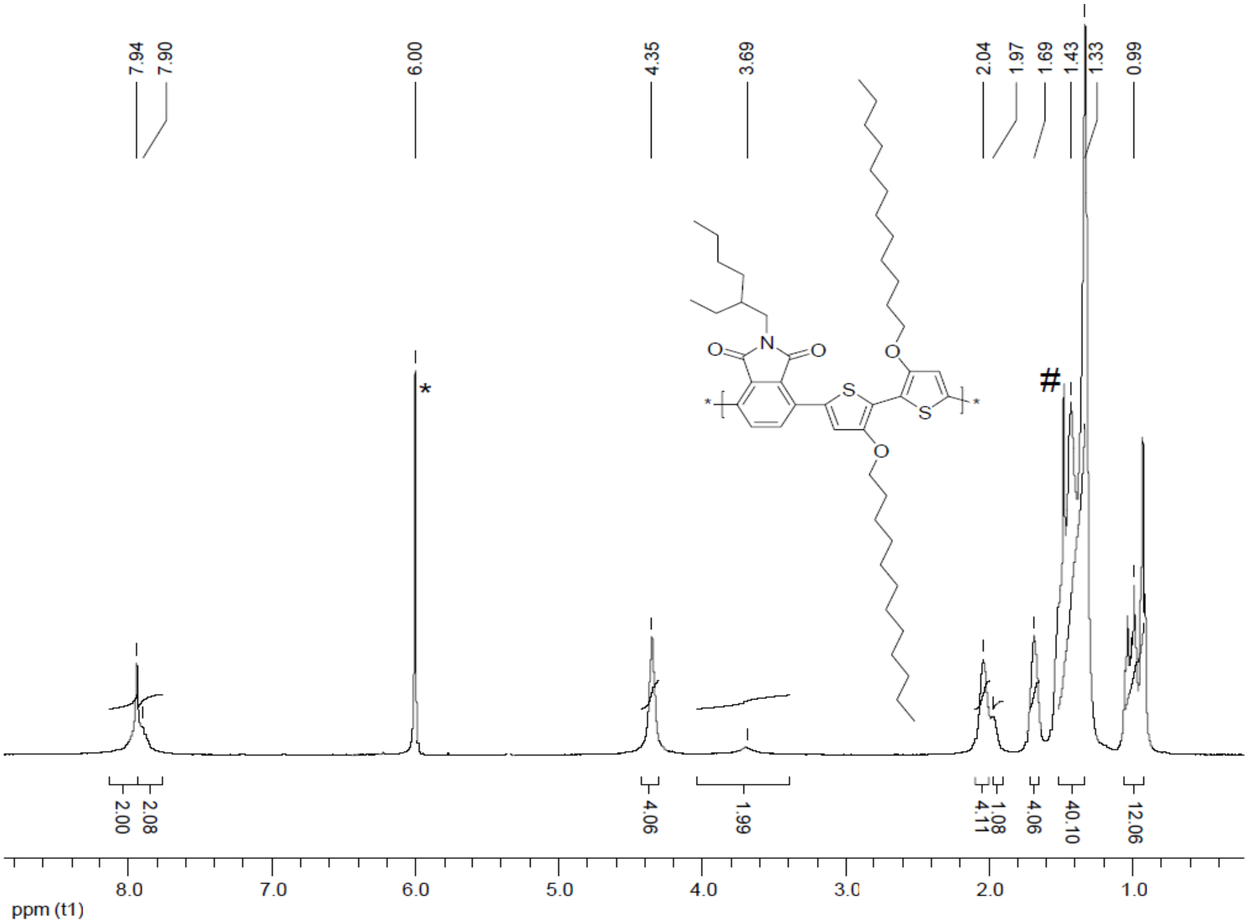


Figure S6. ^{1}H NMR spectrum of **PhBTEH** (100 ºC, in $C_2D_2Cl_4$, *: solvent, #: H_2O)

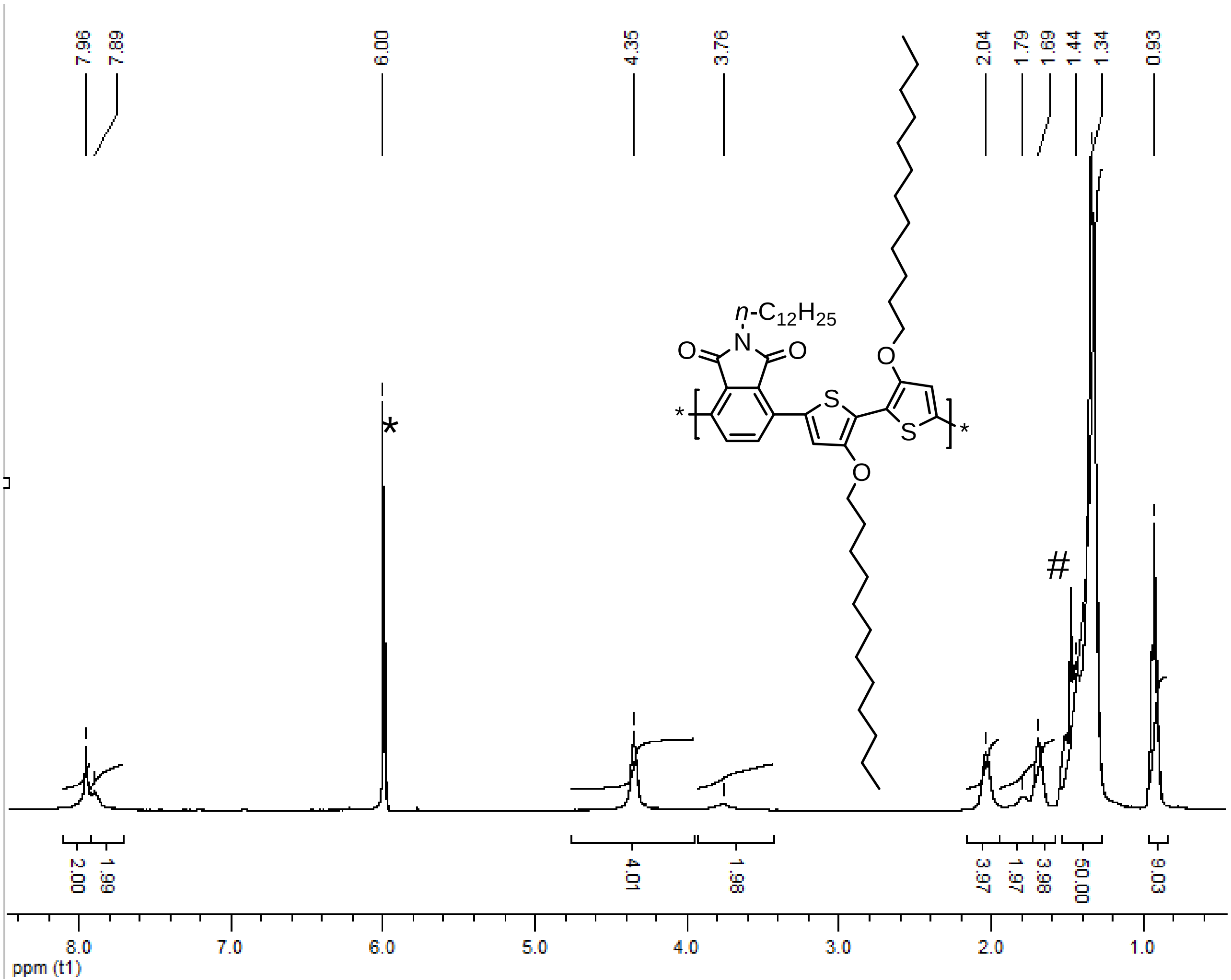


Figure S7. ^{1}H NMR spectrum of **PhBT12** (100 ºC, $C_2D_2Cl_4$, *: solvent, #: H_2O)

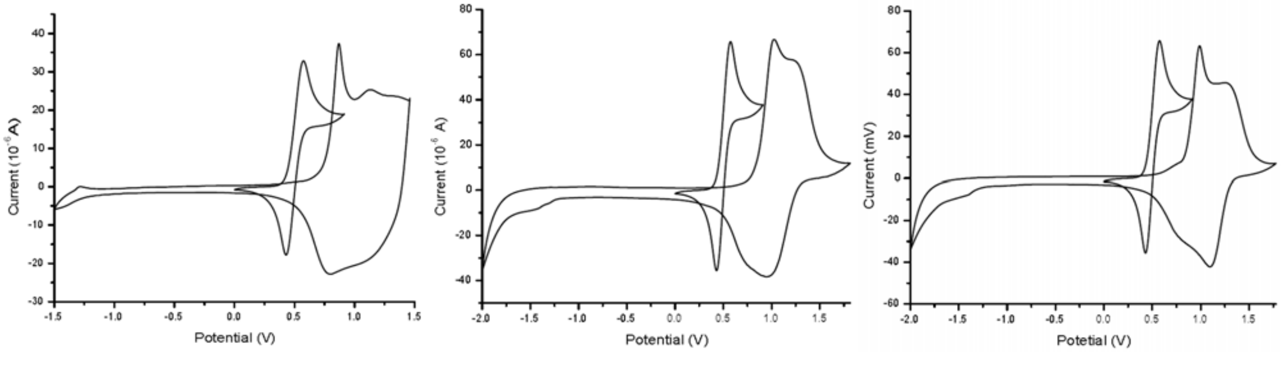


Figure S8. Cyclic Voltammograms of rr-P3HT (left), polymer **PhBTEH** (middle) and **PhBT12** (right**).** Conditions: 0.1 M (n-Bu)$_4$N·PF$_6$ in acetonitrile; working electrode, Pt; counter electrode, Pt wire; reference electrode, Ag/AgCl; Scanning rate, 50 mV/s. Each voltammogram is overlaid with that of Fc/Fc+. The onset of oxidation (E_{ox}^{onset}) for the **PhBT** polymers is +0.34 V vs Fc/Fc+. This value can be compared to that reported for the parent polymer poly(3,3′-dialkoxy-2,2′-bithiophene), which is **PhBT** minus the phthalimide units. The E_{ox}^{onset} for the parent is -0.12 vs SCE = -0.5 vs Fc/Fc+.[6,7] Therefore, the E_{ox}^{onset} for the **PhBT** polymers is 0.8 V more positive than that reported for the parent.

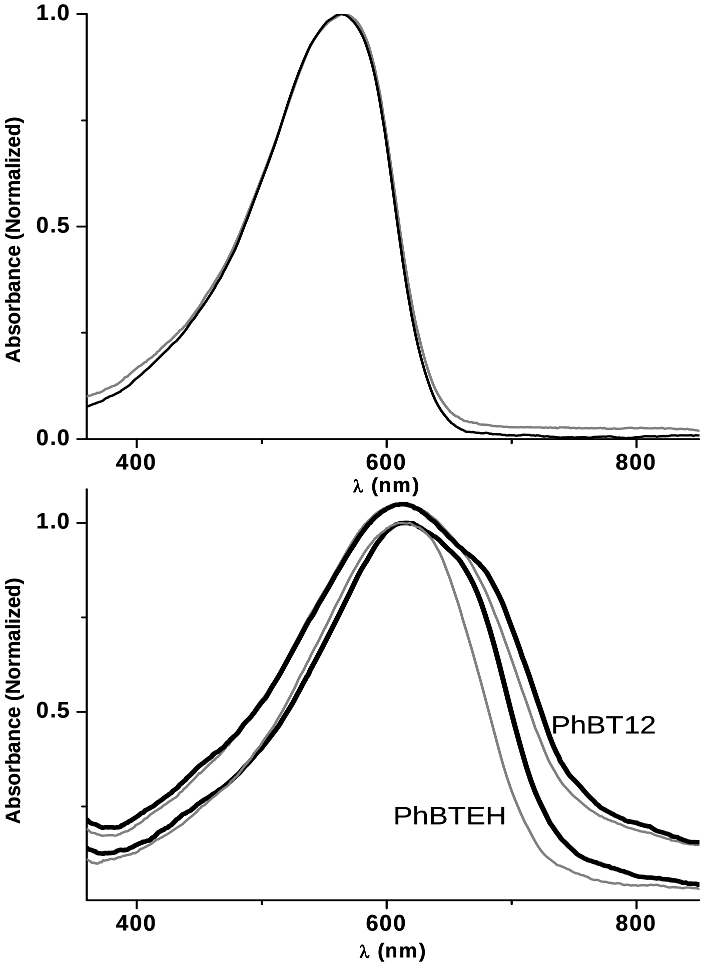


Figure S9. UV-Vis absorption spectra of **PhBT** polymers in chloroform (10^{-5} M, top), and thin films (bottom: grey = as cast, black = annealed 200 °C). Low-energy shoulders develop in the absorption profiles of both polymer films after annealing.

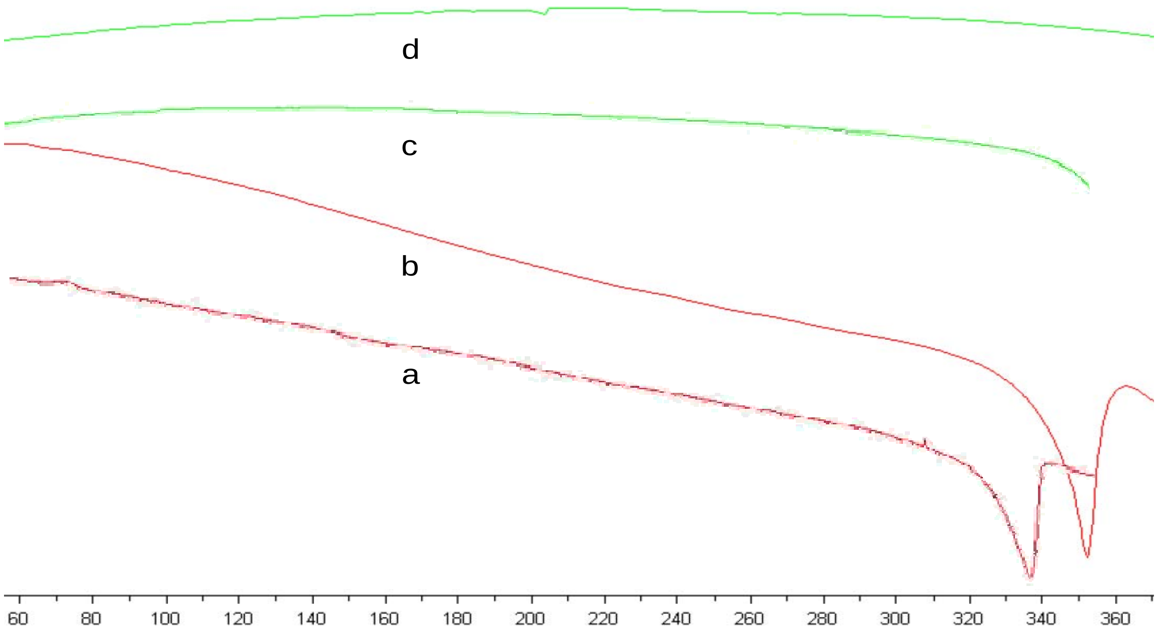


Figure S10. DSC thermograms during first heating and cooling scans (10 ºC/min) of **PhBT** polymers. The endotherms seen on the first heating are not seen in subsequent heating scans. (a) **PhBTEH** heating, (b) **PhBT12** heating, (c) **PHBTEH** cooling, (d) **PhBT12** cooling.

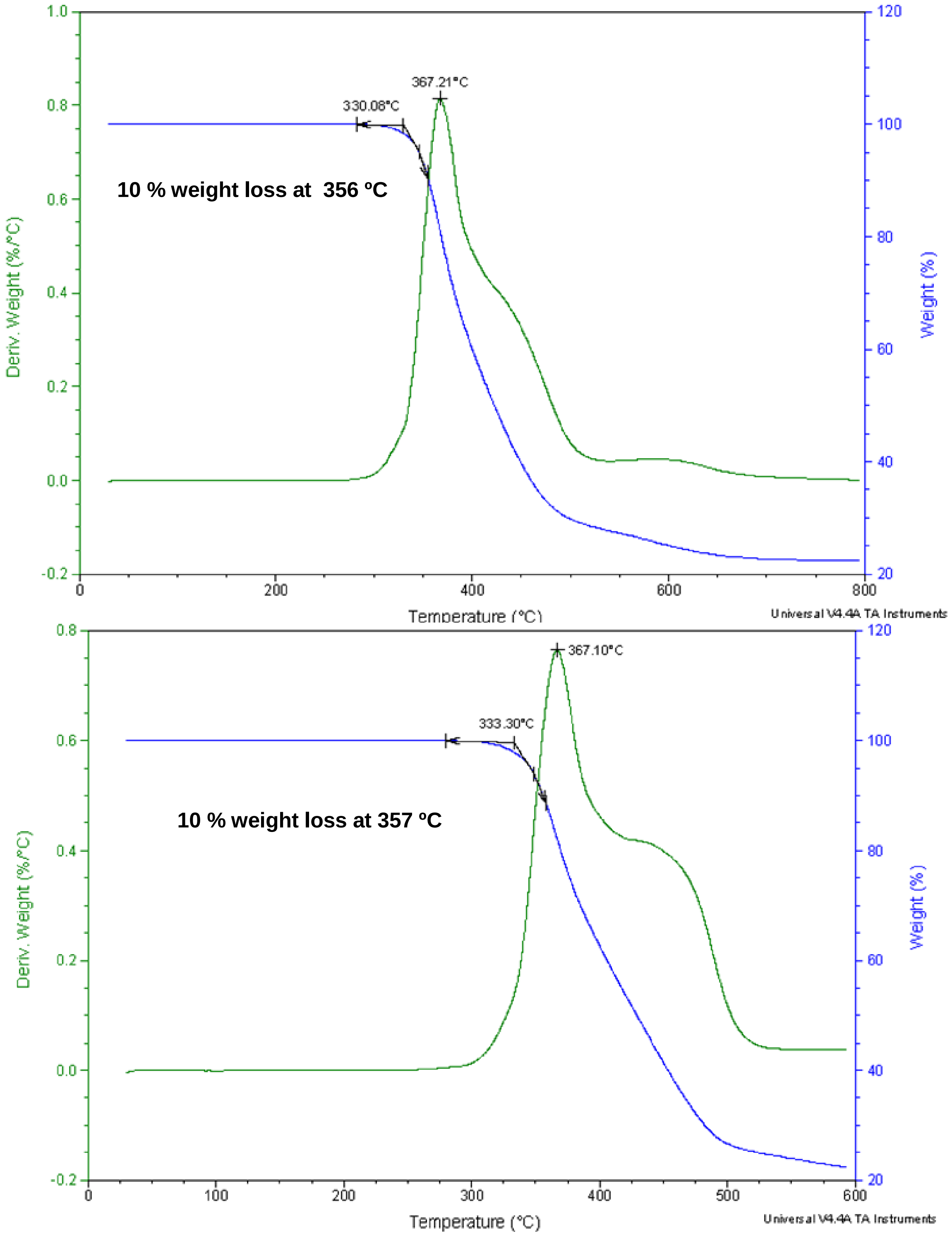
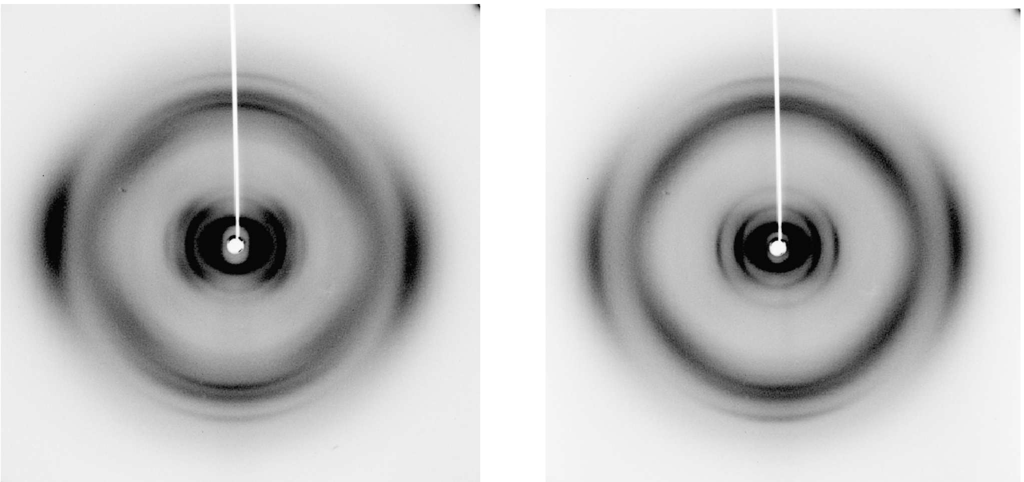


Figure S11. Thermogravimetric analysis (10 ºC/min) of **PhBTEH** (top) and **PhBT12** (bottom). The onsets of weight loss are similar for both polymers and below the 1st order thermal transitions seen in DSC (Figure S10). The nitrogen purge gas used for DSC was UHP grade while that used for TGA was the “bleed-off”, passed through a dryer, from a liquid nitrogen tank.



Polymer	[1,0,0]	[2,0,0]	[3,0,0]	[0,0,1] (π-π)
PhBTEH	25.5	13.2	8.4	3.6
PhBT12	29.8	15.0	10	3.5

Figure S12. Fiber WAXD diffractograms from polymers **PhBTEH** (left) and **PhBT12** (right). Fiber/polymer backbone axes are near vertical. The table summarizes d-spacings in Å and Miller indices assigned to equatorial intensity maxima. d-Spacings indexed as [n,0,0] correspond to lamellar spacings (distances between backbones dictated by side chains) and [0,0,1] is the face-to-face stacking (π-stacking) distance of conjugated backbones. Off-meridianal diffraction maxima, forming hyperbolic layer lines, indicate some degree of 3-dimensional registry for both polymers. These d-spacings vary slightly from those recorded in reflection mode from thin films (see main text).

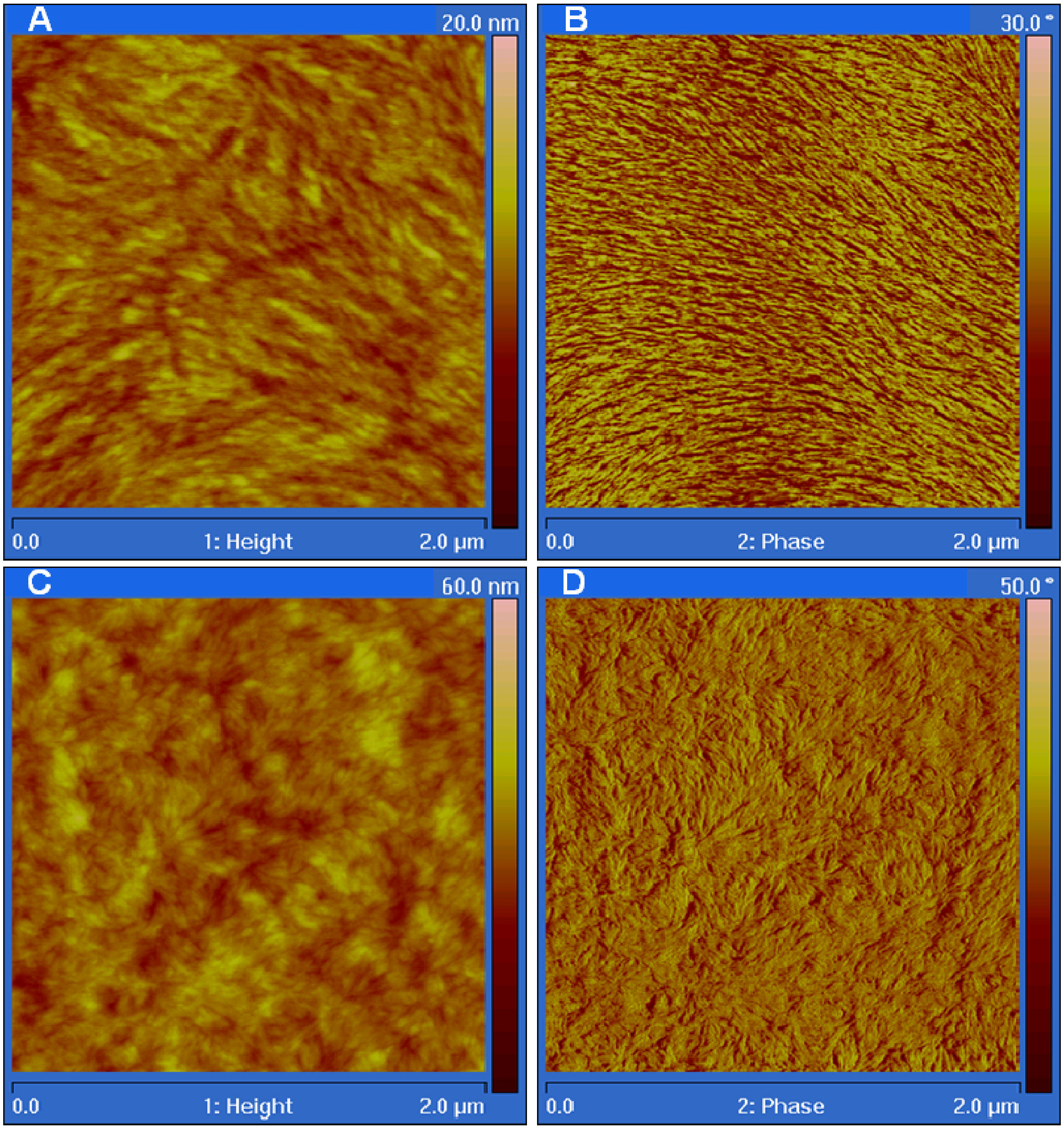


Figure S13. Surface morphology [topography (left) and phase (right)] of **PhBTEH** (A,B), and **PhBT12** (C,D).

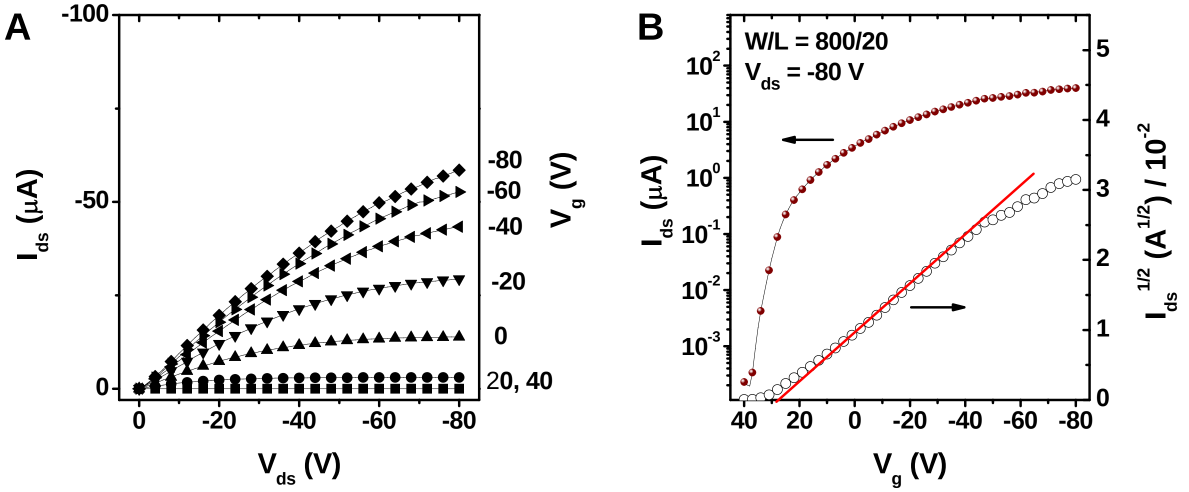


Figure S14. Output (A) and transfer (B) characteristics of **PhBTEH**.

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[7] For conversion factor from SCE to Fc/Fc+, see Pavlischuk, V.V.; Addison, A.W. *Inorg. Chim. Acta* **2000**, *298*, 97-102.