SUPPORTING INFORMATION

Sidechain engineering in poly(2,3-alkylthieno[3,4-*b*]pyrazine)s via GRIM polymerization: Solubility, film formation, and device performance

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Synthetic Methods.

General Information. All materials were reagent grade and used without further purification unless noted. 2,3-Dihexylthieno[3,4-*b*]pyrazine was prepared from 3,4-diaminothiophene as previously reported.[1,2] 3,4-Diaminothiophene was prepared from 2,5-dibromo-3,4-dinitrothiophene[3] as previously reported.[1,2] Poly(2,3-dihexylthieno[3,4-*b*]pyrazine) (PC_6TP) was prepared as previously reported.[4] DMF was dried by mixing with $MgSO_4$ and flushing through a silica gel plug. THF was dried by distillation over sodium/benzophenone. All dry solvents were transferred via standard syringe techniques. All reactions were carried out under a dry nitrogen stream. Reaction glassware was oven dried before use. ^1H and ^{13}C NMR were collected using a 400 MHz spectrometer using $CDCl_3$ as the solvent. NMR peak multiplicity is reported as follows: d = doublet, t = triplet, sept = septet, and m = multiplet. Polymer molecular weights were determined by GPC in reference to polystyrene standards at 110 °C. Samples were prepared in trichlorobenzene (1 mg/mL) and passed through a 0.45 μm filter prior to injection.

2,3-Bis(2-ethylhexylthieno[3,4-*b*]pyrazine (EHTP). The monomer EHTP was prepared as previously reported procedure.[5] 5,10-Diethyl-7,8-tetradecanedione (1.50 g, 5.31 mmol) was dissolved in 50 mL of ethanol. In a separate flask, 3,4-diaminothiophene (3.81 g, 33.4 mmol) was added to 100 mL of ethanol and sonicated until all solids completely dissolved. The two solutions were then combined along with an additional 250 mL of ethanol and the reaction was stirred for 3 h at room temperature. Solvent was then removed at reduced pressure to give a red brown oil. Water was then added, and the mixture extracted with dichloromethane. The organic fractions were combined and dried with magnesium sulfate. Solvent was once again removed by reduced pressure, after which the oil was purified by silica gel chromatography (5% ethyl acetate/hexanes) to give a yellow oil (0.781 g, 40.9%). ^{1}H NMR (CDCl$_3$): δ 7.80 (s, 2H), 2.83 (d, *J* = 7.1 Hz, 4H), 2.04 (sept, *J* = 6.2 Hz, 2H), 1.50-1.25 (m, 16H), 0.94 (t, *J* = 7.3 Hz, 6H), 0.91 (t, *J* = 7.3 Hz, 6H). UV-vis: λ (ε) 297(sh) (6800), 310 (10,400), 319 (10,300), 350 (2000). Cyclic voltammetry: E_{pa}, 1.35 V, $E_{½}$, -2.09 V (ΔE 240 mV). NMR data agree well with previously reported values.[5,6]

5,7-Dibromo-2,3-bis(2-ethylhexyl)thieno[3,4-*b*]pyrazine (Br$_2$EHTP). Br$_2$EHTP was prepared by the modification of a previously reported procedure.[2] 2,3-Bis(2-ethylhexyl)thieno[3,4-*b*]pyrazine (EHTP) (1.57 g, 4.35 mmol) was added to a 500 mL three-neck round-bottom flask equipped with an addition funnel. Dry DMF (130 mL) was added, and the solution was cooled to -78 °C in an acetone/dry ice bath. In a separate flask, NBS (1.94 g, 10.9 mmol) was dissolved in dry DMF (45 mL) and put under dry N$_2$. The NBS solution was added dropwise to the EHTP solution (ca. 30 min addition). The mixture was then warmed to -20 °C in a brine/dry ice bath and stirred for 3.5 h. The mixture was poured onto ice and stirred until the ice melted. Brine was then added, and the mixture was extracted with ethyl acetate. The organic fractions were combined, washed with water, dried with Na$_2$SO$_4$, filtered, and concentrated to give a brown oil. The crude product was purified with a short silica gel plug (80:20 hexanes:DCM) to give a yellow-orange oil (1.51 g, 67%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 2.82 (d, *J* = 7.0 Hz, 4H), 2.02 (sept, *J* = 6.1 Hz, 2H), 1.45–1.23 (m, 16H), 0.90 (t, *J* = 7.4 Hz, 6H), 0.87 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (CDCl$_3$, 400 MHz): δ 158.0, 139.2, 103.2, 39.6, 38.0, 32.8, 28.9, 26.1, 23.1, 14.2, 11.0. NMR data agree well with previously reported values.[6]

Poly(2,3-bis(2-ethylhexyl)thieno[3,4-*b*]pyrazine) (PEHTP). PEHTP was prepared by the modification of a previously reported procedure.[4] To a 50 mL three neck round bottom flask equipped with a condenser was added, Br$_2$EHTP (0.95 g, 2.05 mmol) and dry THF (10 mL). Methylmagnesium bromide (0.7 mL, 3.0 M solution in diethyl ether) was added via syringe dropwise. The reaction was heated at reflux for 1 h. Ni(dppp)Cl$_2$ (0.0054 g, 0.010 mmol) was added, and the reaction was heated at reflux for another 1 h. The reaction was let cool to room temperature and precipitated by adding dropwise via Pasteur pipette to MeOH (~100 mL) at 0 °C. The mixture was stirred at 0 °C for 2 h. The precipitate was loaded onto a glass frit and washed with methanol via Soxhlet apparatus for 24 h. The soluble fraction was extracted with $CHCl_3$ and concentrated to give a purple-black solid. The solid was pumped for 4 h to yield the desired product (0.49 g, 68%). ^1H NMR ($CDCl_3$, 400 MHz): δ 3.14, 2.03, 1.47, 1.24, 0.95, 0.83. GPC: $M_w = 10300$, $M_n = 7400$, PDI = 1.39.

UV-visible-NIR Spectroscopy.

Absorption spectroscopy measurements were collected using a dual beam scanning spectrophotometer. Solution spectra were collected from dilute $CHCl_3$ solutions in 1 cm quartz cuvettes. Spin-coated polymer films on glass plates were used for solid-state analysis. Optical bandgaps were determined from the solid-state spectra by extending the steepest part of the low energy absorption onset to the baseline.

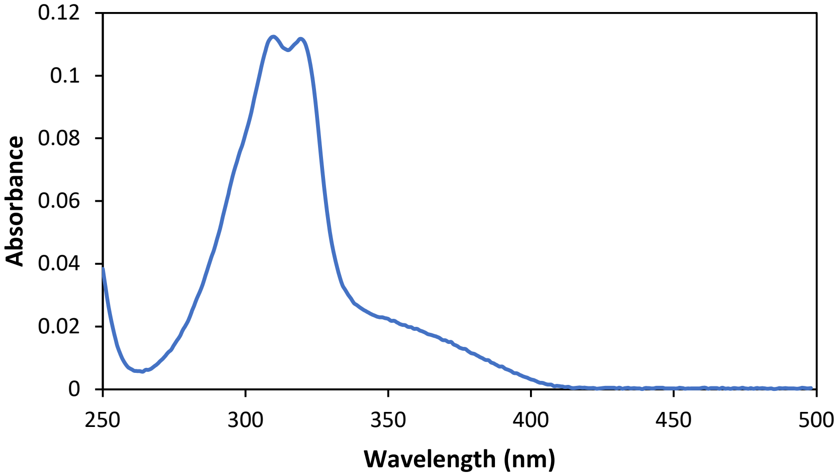

Figure S1. Absorption spectra of EHTP in chloroform

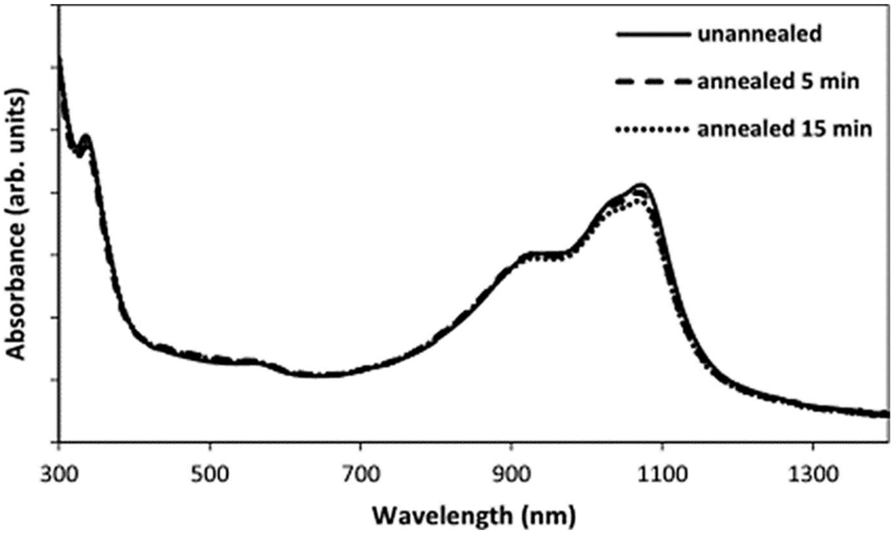

Figure S2. Absorption spectra of unannealed and annealed PEHTP:PCBM 1:1 films spun from chlorobenzene

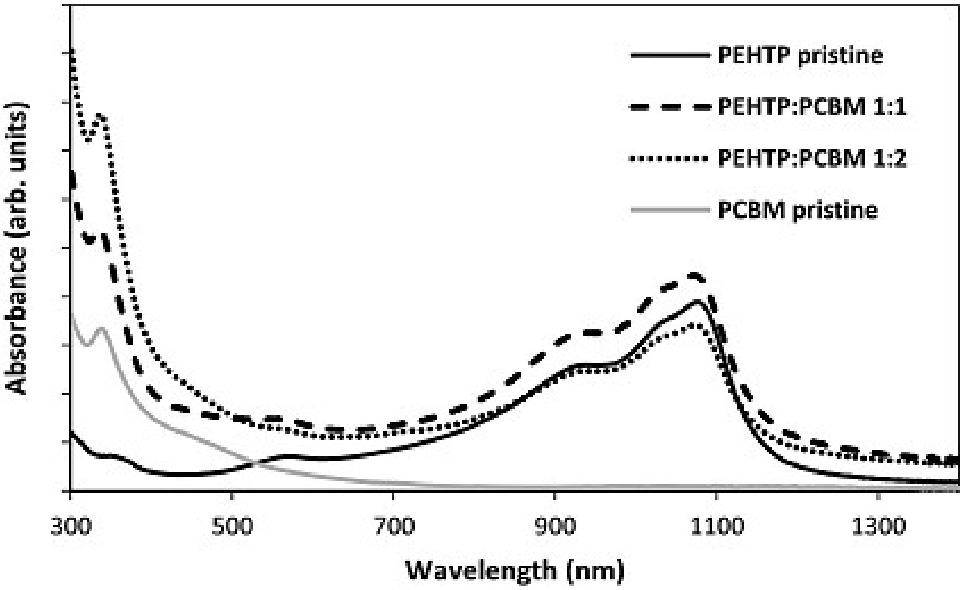

Figure S3. Thin film absorption spectra of pristine PEHTP, pristine PCBM, and blends of PEHTP:PCBM

Electrochemistry.

Electrochemical analysis was performed using a three-electrode cell with a platinum disc working electrode and a platinum wire auxiliary electrode. The Ag/Ag$^+$ reference electrode (0.251 V vs. SCE) was prepared with a 0.01 M $AgNO_3$ and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution in dry MeCN.[7] MeCN used for electrochemistry was dried by distillation over CaH_2 under dry N_2. Polymer films were prepared by drop casting a polymer solution in $CHCl_3$ onto the working electrode. Electrochemical cells were oven dried. Solutions of 0.10 M $TBAPF_6$ in dry MeCN were deoxygenated by sparging with argon before each scan and blanked with argon during the scan. Measurements were taken with a sweep rate of 100 mV s^{-1}. HOMO and LUMO energy levels were estimated by taking the onsets of first oxidation and reduction and referencing to ferrocene (5.1 V vs. vacuum).[8]

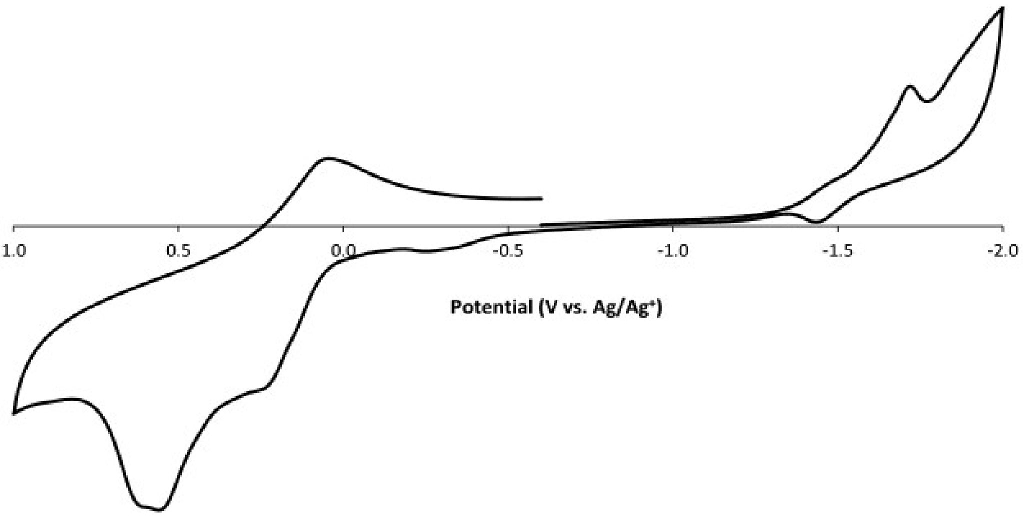

Figure S4. Cyclic voltammogram of PEHTP

Device fabrication and characterization.

Patterned ITO glass slides were cleaned via sonication in detergent, acetone, and isopropyl alcohol, followed by ozone treatment. PEDOT:PSS layers were spin coated onto the ITO slide and annealed at 140 °C for 30 minutes. Solutions of PEHTP:PCBM in chloroform, chlorobenzene, or 1,2-dichlorobenzene were prepared and spin coated under nitrogen atmosphere (active layer with a thickness was 85–140 nm). If annealed the active layer was annealed under nitrogen atmosphere at 140 °C. A layer of ZnO was spin coated and annealed at 90 °C for 5 minutes under nitrogen atmosphere. The aluminum cathode was thermally deposited in a vacuum deposition chamber to give a thickness of ~100 nm.

Table S1. OPV data for PEHTP:PCBM devices

PEHTP:PCBM	**Solvent**[a]	**Annealing**	**V_{OC} (V)**	**J_{SC} (mA cm^{-2})**	**Fill Factor**	**PCE (%)**
1:1	CF	5 min	0.26	-0.68	0.47	0.082
1:1	CB	unannealed	0.25	-1.82	0.51	0.229
1:1	CB	5 min	0.24	-1.03	0.53	0.131
1:1	CB	15 min	0.23	-0.95	0.53	0.116
1:2	CB	5 min	0.24	-1.12	0.53	0.144
1:2	CB	15 min	0.24	-1.09	0.54	0.140
1:1	DCB	unannealed	0.24	-1.34	0.48	0.152
1:1	DCB	5 min	0.24	-1.58	0.49	0.185

[a] chloroform (CF), chlorobenzene (CB), dichrlobenzene (DCB)

The external quantum efficiency (EQE) measurements were conducted using a chopped halogen lamp source coupled through an Oriel Cornerstone scanning monochromator. The output 2 nm bandwidth monochromatic light is then coupled via a quartz fiber bundle into the glovebox where it is then focused to illuminate the cell area with no overfilling. At higher wavelengths order sorting filters were used to remove lower wavelengths from the broadband input light. The illuminated device output electrodes are connected to a Stanford Research Systems SR830 lock-in amplifier. A reference diode measuring a reflection off a glass wedge is used to monitor any source intensity fluctuations. The monitor data is acquired by a separate Stanford Research Systems SR830 lock-in amplifier that allows absolute spectral corrections via a look-up table, which is generated from a reference scan performed prior to the measurement of the EQE. Output signals from both phase-locked loop measurements are recorded on a PC as is the illumination wavelength.

The noise floor measurement was performed using a B1500A Semiconductor Device Analyser with a medium power source measure unit (SMU) B1511B as described elsewhere.[10] The dark current obtained was fast Fourier transformed via Matlab to give the graph presented below.

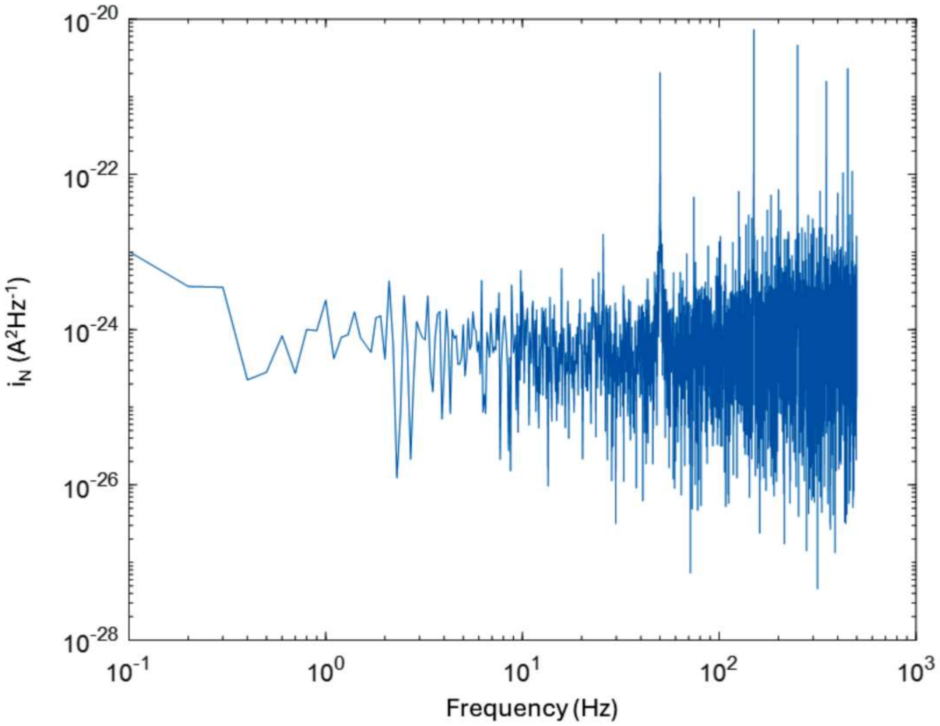

Figure S5. Fourier transformed dark current of 1:1 PEHTP:PCBM device.

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