Side Chain Engineering of Fused Aromatic Thienopyrazine based Low Band-gap Polymers for Enhanced Charge Carrier Mobility

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Supporting Information

General Experimental Methods. ^{1}H and ^{13}C NMR spectra were recorded using Varian Inova 300, Merc 400 or Inova 500 in $CDCl_3$ at 293 K. Gel Permeation Chromatography (GPC) was performed in THF. The molecular weights were calculated using a calibration curve based on polystyrene standards. Thermal gravimetric analyses (TGA) were performed using a Mettler TOLEDO TGA/SDTA 851e at a heating rate of 10 ^{o}C/min under a nitrogen flow of 20 mL/min. Electrochemical analysis of the polymers was carried out by cyclic voltammetry using a CHI411 instrument from CH Instruments, Inc. The experiments were performed under a stream of argon in a saturated solution of 0.05 M tetra-*n*-butylammonium hexafluorophosphate (n-Bu_4NPF_6, from Strem Chemicals, Inc., recrystallized from ethanol) as a supporting electrolyte in anhydrous ODCB. The experiments were carried out using platinum electrodes at a scan rate of 100 mVs^{-1} against Ag wire as a pseudoreference electrode at rt. Ferrocene was used as a reference oxidation potential for all of our compounds. UV-vis-NIR absorption spectra were recorded in ODCB in a UV-vis spectrophotometer (model Cary 6000i) at rt. using a quartz cuvette with a path length of 1 cm. Thin film for UV-vis in solid state was prepared by drop casting. Optical bandgaps were calculated from the edge of the visible-absorption bands from film spectra. HOMO of the polymers were estimated from photoelectron spectroscopy of the thin films.

3,4-diaminothiophene dihydrochloric acid salt was purchased from Acros Organics. 2-(3-alkyl-2-thienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes were prepared according to the reported procedures.[32] 3,6-Dibromophenanthrene-9,10-dione (**3**) was synthesized according to a literature reported procedure. Tetrahydrofran (THF), N,N-dimethylformamide (DMF), and toluene were purified through the Pure Sol-MD Standard Design Solvent Purification System, Innovative Technology Inc. Dimethoxyethane (DME) was purchased from Acros Organics. Acenaphtoquinone, tetrakis(triphenylphosphine)palladium (0), N-bromosuccinimide (NBS), Aliquot336, chlororbenzene, and *o*-dichlorobenzene were purchased from Aldrich or Alfa Aesar and used without further purification.

GIXD data was taken at the Stanford Synchrotron Radiation Lightsource beam line 11-3 using a wavelength of 0.9752 Å and an area detector. OTFT transfer and output characteristics were recorded in air using a Keithley 4200 semiconductor parametric analyzer (Keithley Instruments, Cleveland OH). Tapping mode AFM investigation of the films was done using a Multimode Nanoscope III with Extender electronics (Digital Instruments/Veeco Metrology Group, Santa Barbara, CA). Thickness measurements were performed with a Dektak 150 profilometer (Veeco Metrology Group).

Fabrication of OTFT Devices.

Surface modification of SiO_2 substrates. OTS device substrates we used highly doped n-type (100) Si wafers (< 0.004 Ωcm) with a 300 nm dry thermal oxide gate dielectric (capacitance C_i=10 nFcm^{-2}). These wafers were cleaned in piranha solution (highly corrosive and oxidizing 7:3 mixture of H_2SO_4 and H_2O_2) for 30 min, rinsed with dionized water and dried under a nitrogen stream. For OTS treatment, a 0.1 % solution of octadecyltrimethoxysilane (Gelest Inc., Morrisville, PA) in trichloroethylene (EMD Chemicals Inc., Darmstadt, Germany) was spin-coated on the cleaned wafers, allowed to react overnight at room temperature in the presence of ammonia vapor. Excess silane was removed by ultrasonication in toluene, followed by rinsing with toluene, acetone and isopropyl alcohol, and drying under a stream of nitrogen. OTS-treated wafers typically showed contact angle ~ 99°.

Transistor fabrication and testing. Inside a glove box with dry N_2 environment we prepared 1 mg/mL solutions of the 5 different semiconductor copolymers in 1-2 dichlorobenzene (ODCB), and filtered them through 0.2 μm pore PTFE syringe filters. We applied enough solution to cover the modified SiO_2 substrates, and enclosed them in a glass chamber at 110 °C saturated with ODCB vapor, to achieve slow evaporation (~20 min). The films were then dried on a hot plate at 80°C for 30 min. After drying, some films were further annealed at different temperatures and for different amounts of time. The 40 nm gold contacts evaporated through a shadow mask had a W/L = 20, with L= 50 μm.

Solar Cell Fabrication and Characterization

Bulk heterojunction solar cells were prepared by spin coating mixtures of polymer and [6,6]-phenyl C_{61}-butyric acid methyl ester ($PC_{[61]}BM$) dissolved in 1,2-ortho-dichlorobenzene (ODCB). Glass substrates coated with indium tin oxide (Thin Film Devices) served as device substrates. After cleaning the substrates by standard methods, a 50 nm layer of poly3,4-ethylenedioxythiophene polystyrenesulfonate (PEDOT-PSS) with a resistivity of 1 kΩ cm was deposited in air by spin coating. All subsequent processing and testing occurred in a nitrogen environment with oxygen levels maintained at less than 5 ppm. Polymer- $PC_{[61]}BM$ solutions were then spun at 900 rpm for thickness of 110 nm and allowed to solvent anneal in a closed Petri dish. Aluminum electrodes with thicknesses between 75 and 100 nm were deposited by thermal evaporation at pressures of 10^6-10^5 Torr. After electrode deposition, IV characteristics were recorded in the dark and under simulated 1 sun AM 1.5 radiation with a Keithley 2400 source meter. Illumination was achieved with a 91160 300 W Oriel solar simulator equipped with a 6258 ozone-free Xe lamp and an air mass AM 1.5 G filter.

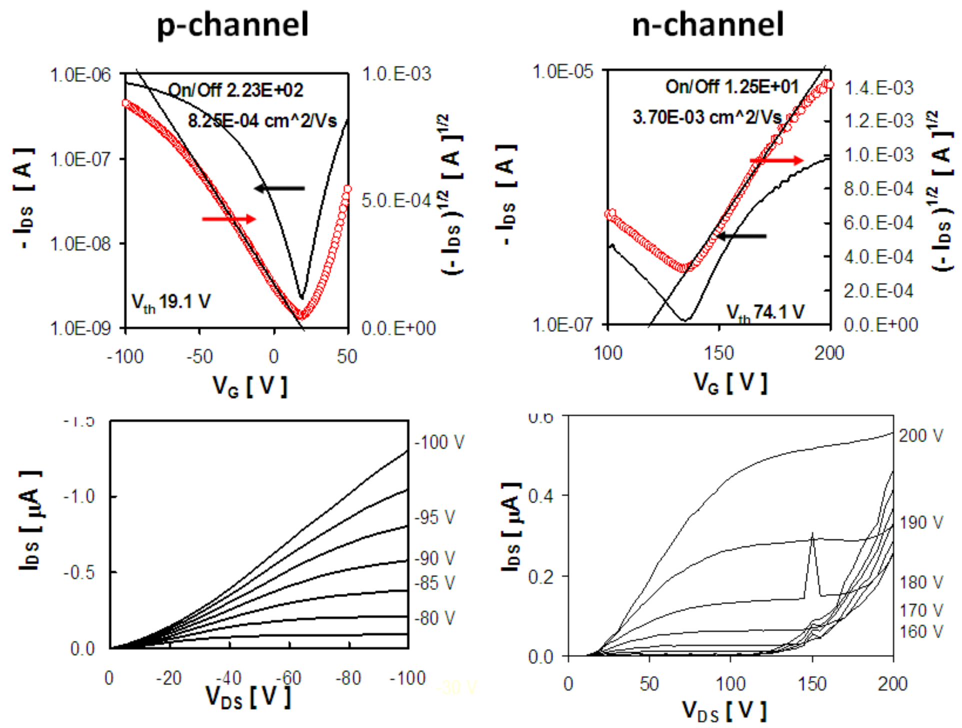

Figure S1. Representative I-V and output curves of *p*-type and *n-type* OTFTs of **PHEH-EHF** tested in the inert and dry atmosphere (glove box).

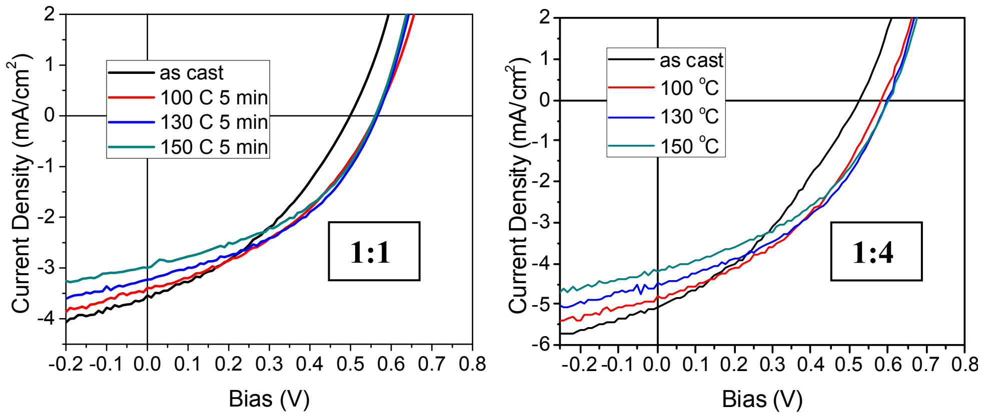

Figure S2. I-V characteristics under AM1.5 illumination for the solar cell fabricated from **PHEH-EHF** (polymer blend with PC[61]BM) at different annealing condition.

Table S1. Solar cell data of **PHEH-EHF** at different condition

Acceptor	**Blend ratio**	**Annealing condition**	**Jsc mA/cm^2**	**Voc V**	**FF**	**PCE %**
PC[61]BM	**1:1**	**As cast**	3.55	0.495	0.38	0.67
		100 °C	3.38	0.565	0.40	0.76
		130 °C	**3.23**	**0.565**	**0.43**	**0.78**
		150 °C	3.00	0.565	0.43	0.73
	1:4	**As cast**	5.13	0.525	0.35	0.94
		100 °C	4.80	0.585	0.40	1.12
		130 °C	**4.50**	**0.595**	**0.43**	**1.15**
		150 °C	4.20	0.605	0.41	1.04

Table S2. Photovoltaic properties of the Bulk Heterojunction Solar cells of the Polymers.

Polymer	Acceptor	Blending ratio	J_{sc} mA/cm^2	V_{oc} V	FF	PCE %
EHPH-EHF	PC[61]BM	1:4	2.28	0.485	0.52	0.57
PHD-DF[a]	PC[61]BM	1:4	1.72	0.495	0.50	0.43
		1:1	2.18	0.505	0.50	0.55
PHEH-EHF[b]	PC[61]BM	1:4	4.50	0.595	0.43	1.15
		1:1	3.23	0.565	0.43	0.78

[a] Annealed at 100°C and [b] annealed at 130°C