Thiophene Rich Fused-aromatic Thienopyrazine Acceptor for Donor-acceptor Low Band-gap Polymers for OTFT and Polymer Solar Cell Applications

Rajib Mondal,[1] Hector A. Becerril,[1] Eric Verploegen,[1,4] Dongwook Kim,[2] Joseph E. Norton,[2] Sangwon Ko,[1] Nobuyuki Miyaki,[1] Sangjun Lee,[3] Michael F. Toney,[4] Jean-Luc Brédas,[2] Michael D. McGehee,[3] and Zhenan Bao[1,]*

[1]Department of Chemical Engineering, Stanford University, Stanford CA, 94305.

[2]School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, GA, 30332.

[3]Department of Materials Science, Stanford University, Stanford CA, 94305.

[4]Stanford Synchrotron Radiation Lightsource, Menlo Park, CA, 94025.

E-mail: zbao@stanford.edu

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] 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.

Film Thickness measurements were performed with a Dektak 150 profilometer (Veeco Metrology Group).

GIXD data was taken at the Stanford Synchrotron Radiation Laboratory using a wavelength of 0.9752 Å and an area detector.

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. Device thicknesses were measured with a Dektak profilometer.

Table S1. Calculated π-π stacking distances of four possible orientations of each donor-acceptor monomer unit.

Polymer / Orientation	**BDTdn-FL**		**BDTup-FL**		**BDTdn-CPDT**		**BDTup-CPDT**	
	π- π stacking (Å)							
	End 1	End 2	End 1	End 2	End 1	End 2	End 1	End 2
Orientation 1	3.297	3.806	3.493	3.417	3.500	4.456	3.604	4.344
Orientation 2	3.316	4.796	3.325	4.710	3.336	3.852	3.343	3.876
Orientation 3	3.677	2.853	3.702	2.905	3.896	4.574	3.907	4.511
Orientation 4	3.825	3.825	3.707	3.707	3.570	3.608	3.579	3.633
Different orientations are presented in Figure S1.								

Table S2. Calculated electronic coupling and relative energies of four possible orientations of each donor-acceptor monomer unit.

Polymer / Orientation	**BDTdn-FL**		**BDTup-FL**		**BDTdn-CPDT**		**BDTup-CPDT**	
	V_{ij} (meV)	ΔE (meV)	V_{ij} (meV)	ΔE (meV)	V_{ij} (meV)	ΔE (meV)	V_{ij} (meV)	ΔE (meV)
Orientation 1	4.91	100.82	-3.22	118.89	-3.33	90.31	9.68	103.00
Orientation 2	-120.56	0.00	-123.49	0.00	-107.18	0.00	106.34	0.00

Orientation 3	-93.88	126.04	-22.39	106.91	-86.84	94.40	93.34	93.93
Orientation 4	49.93	115.13	-66.36	89.17	17.88	85.99	8.91	90.86
Different orientations are presented in Figure S1.								

Table S3. Oligomer Energy Levels Calculated as the B3LYP/6-31G(d,p) Gas-Phase HOMO and LUMO Levels, Adiabatic Values Calculated from Optimized Structures on the Neutral and Ionic Potential Energy Surfaces, and Vertical Transition Energies to the Lowest S1 State Calculated with the TDDFT Method.

	n	HOMO	LUMO	IPadiabatic	EAadiabatic	S0→S1
AC-FL	1	-4.60	-2.39	5.50	1.42	1.90
	2	-4.46	-2.46	5.07	1.83	1.71
	3	-4.42	-2.49	4.91	2.00	1.64
PH-FL	1	-4.59	-2.64	5.49	1.66	1.66
	2	-4.47	-2.70	5.07	2.07	1.50
	3	-4.43	-2.73	4.91	2.23	1.43
BDTdn-FL	1	-4.54	-2.76	5.43	1.77	1.46
	2	-4.40	-2.81	5.01	2.16	1.32
	3	-4.36	-2.83	4.84	2.33	1.26
BDTup-FL	1	-4.58	-2.74	5.48	1.75	1.56
	2	-4.46	-2.79	5.07	2.15	1.41
	3	-4.42	-2.82	4.91	2.32	1.34

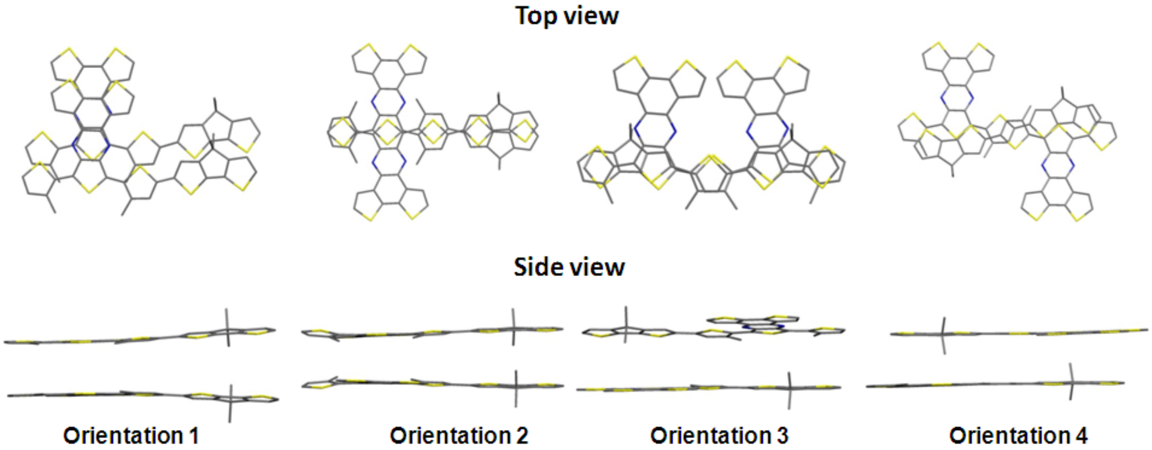

Figure S1. Four different orientations of **BDTdn-FL** (top view and side view); monomer model systems calculated at the B3LYP/6-31G(d,p) level of theory (similar orientations of the monomer units were considered for **BDTup-FL, BDTdn-CPDT,** and **BDTup-CPDT**).

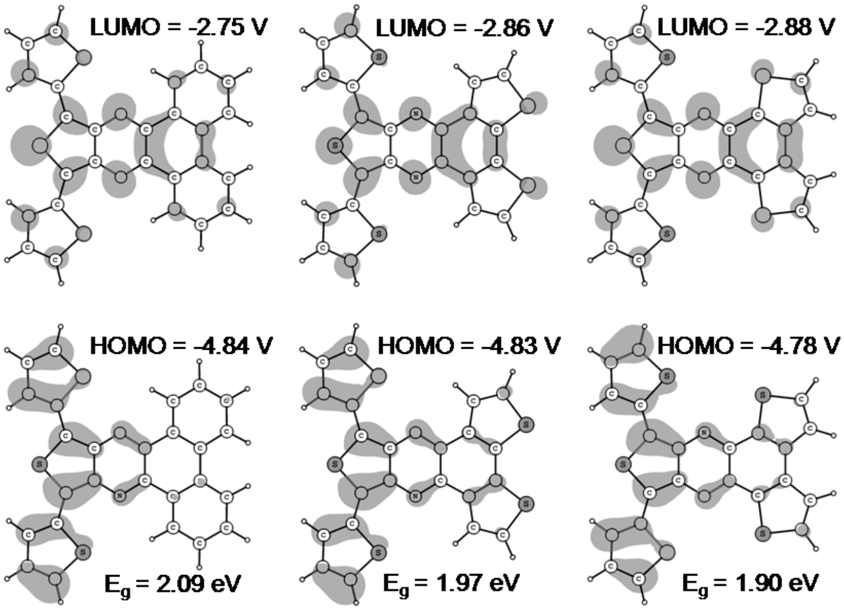

Figure S2. HOMO and LUMO wave-functions of the phenanthrene and benzodithiophene based thienopyrazine monomers, calculated at the B3LYP/6-31G(d,p) level of theory.

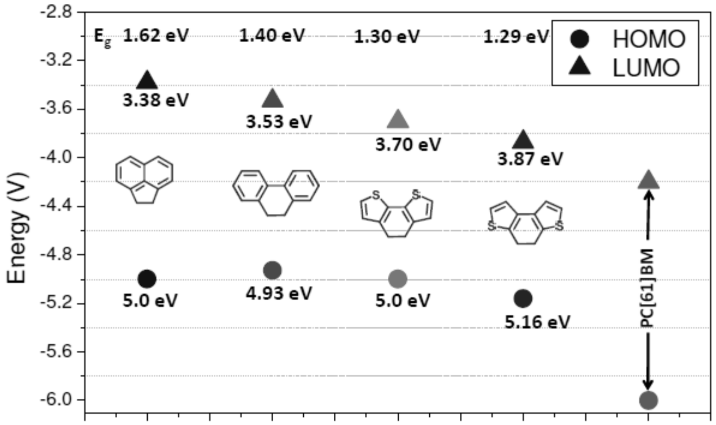

Figure S3. Relative HOMO and LUMO energy levels, band gaps of **AC-FL**, **PH-FL**, **BDTdn-FL**, and **BDTup-FL** (acenaphthyl, phenanthrene, and benzodithiophene based **FL** copolymers).

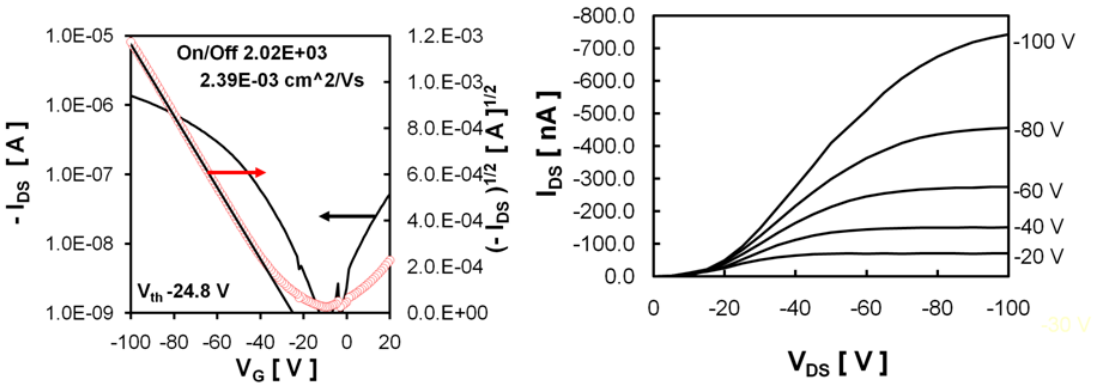

Figure S4. Representative I-V and output curves of *p*-type OTFTs of **BDTup-FL** tested in the inert and dry atmosphere (glove box).

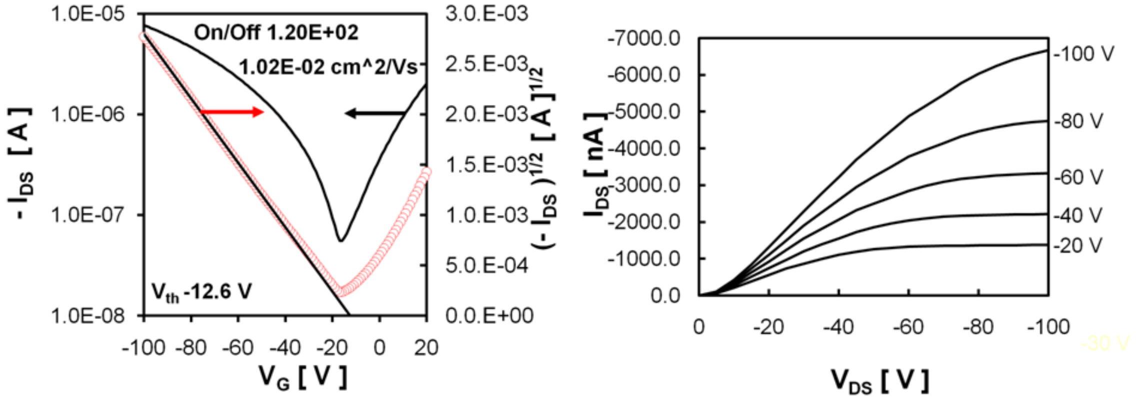

Figure S5. Representative I-V and output curves of *p*-type OTFTs of **BDTup-CPDT** tested in the inert and dry atmosphere (glove box).