Transistor and Solar Cell Performance of Donor-Acceptor Low Bandgap Copolymers Bearing an Acenaphtho[1,2-*b*]thieno[3,4-*e*]pyrazine (ACTP) Motif

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Supporting Information
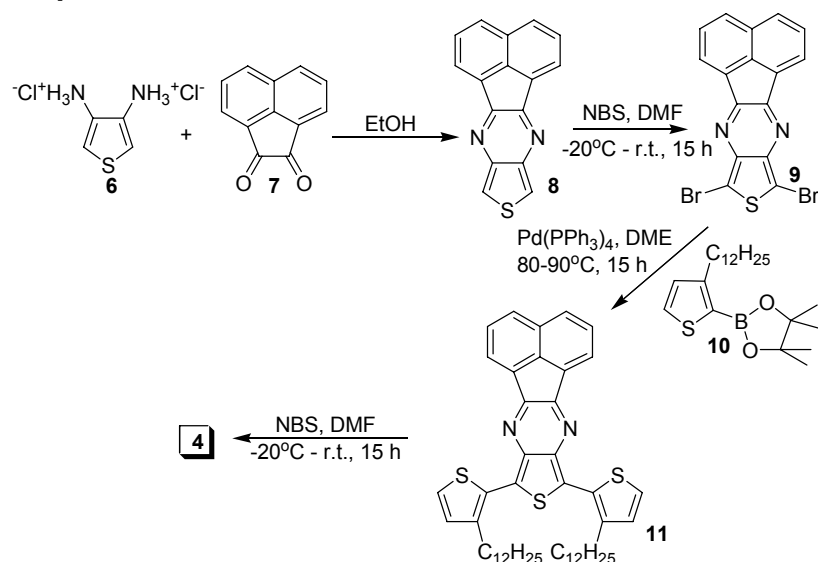
Preparation of ACTP Monomer

Figure S1. Synthesis of ACTP acceptor unit.

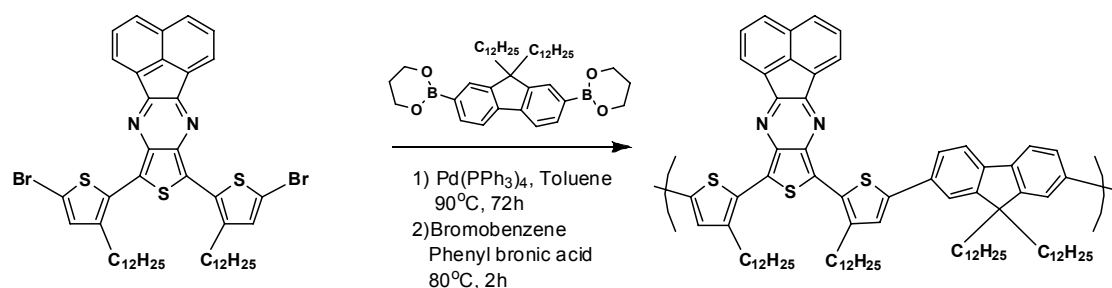## *Copolymerization Conditions*

Figure S2. Synthetic procedure.

To an equimolar mixture of donor and and acceptor precursors (0.163mmol), we added tetrakis(triphenylphosphine)palladium (5.8mg, mmol), Aliquot336 (0.03g, mmol), and 3mL of chlorobenzene, toluene, or 1,2-dichlorobenzene as solvent. Potassium carbonate in aqueous solution was added under argon flow. The mixture was degased three times, heated to 90°C, stirred for 12 hours and the reaction was quenched with phenyl boronic acid and bromobenzene.

The crude copolymer was recovered after precipitation with a mixture of methanol and 30% NH_4OH in aqueous solution and washed with water, methanol, acetone, and hexane. This material was redissolved in heated (90°C) o-dichlorobenzene with a palladium scavanger and stirred for 2h to remove traces of Pd metal from the copolymer.

Finally the copolymer was precipitated by filtering the o-dichlorobenzene solution through a 0.2 μm PTFE filter into a methanol bath, and dried under reduced pressure. All copolymer materials were stored in dry N_2 enviroment. The materials were analyzed by gel permeation chromatography (GPC, see **Table 1** in manuscript) and by differential scanning calorimetry (DSC). **Fig. S3** shows the almost featurless DSC of the lightest and the heaviest copolymers (**1** and **4** in the manuscript), both showing weak transitions in the vicinity of 200°C.
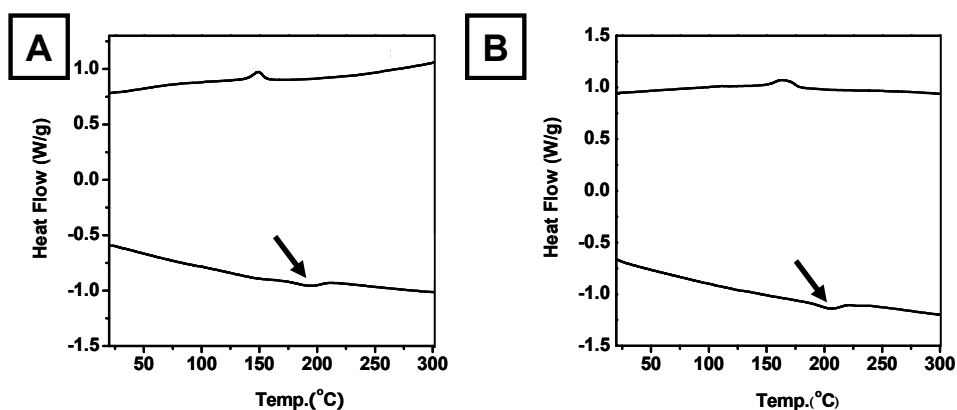
Figure S3. Second DSC scans of copolymers **1** (**A**) and **4** (**B**) 10 kDa and 28 kDa respectively, both showing a small transition around the optimal annealing temperature ~200 °C.

Energy of Frontier Molecular Orbitals.

We measured the HOMO and LUMO energy of our polymers using cyclic voltametry (CV) for polymer solutions and photoelectroscopy (PES) for polymer thin-films. The band-gap energy was estimated from the onset UV-vis absorption. The measurementes cannot be direcly compared because CV measurements were performed in Argon-bubbled solution, while the PES where taken on dry thin films exposed to ambient air.

For CV of polymer solutions we used a a CH Instruments Electrochemical Analyzer, working under a stream of argon in anhydrous 1,2-dichlorobenzene (ODCB) containing 0.05 M, ethanol recrystallized tetra-nbutylammonium hexafluorophosphate as supporting electrolyte. We used platinum electrodes at a scan rate of 100 mVs-1 against Ag wire as a pseudoreference electrode at room temperature. Ferrocene was used as a reference oxidation potential.

For PES of polymer thin-films we used a Riken Keiki Model 2 work-funtion analyzer, working in ambient conditions, with a pure gold standard. The LUMO of the thin-films cannot be

directly measured by PES, and has to be estimated from the optical bandgap, which leads to inevitable inaccuracy, but is meant to be used as a first approximation.

Table S1. HOMO and LUMO energies of the ACTP-DAF copolymers.

Polymer	Solution (ODCB)						Film (solid state)				
	UV-vis			CV			UV-vis			PES	
	A max	ε [a]	Eg (eV)	HOMO [b]	LUMO [c]	Eg (eV)	Amax	α	Eg (eV)	HOMO [d]	LUMO [e]
	(nm)	$(M^{-1}cm^{-1})$		(eV)	(eV)		(nm)	(cm^{-1})		(eV)	(eV)
1	333, 417, 586	1.58×10^4	1.7	-4.86	-3.2	1.66	321, 445, 655	-	1.58	-	-
3	333, 420, 635	1.56×10^4	1.6	-	-	-	326, 457, 666	3.37×10^4	1.56	-4.92	-3.36
4	-	-	-	-	-	-	325; 455, 666	5.51×10^4	1.55	-5.00	-3.45
5	331, 423, 612	1.69×10^4	1.7	-4.83	-3.18	1.65	311, 449, 653	3.35×10^4	1.56	-4.94	-3.38

a) Molar absorption coefficient measured at the low-energy absorption maxima.
b) Determined by cyclic voltammetry measurements in 1,2-dichlorobenzene solution based on the oxidation onset value of ferrocene
(HOMO = 4.8 ev).
c) LUMO = Egap(CV) +HOMO.
d) Photoelectron spectroscopy
e) Estimated LUMO = Egap(UV) +HOMO.

Fabrication of OTFT Devices.

Surface modification of SiO$_2$ substrates. OTS and PTS 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°. PTS surfaces were prepared by immersing cleaned wafers in a 3% solution of phenyltriethoxysilane (Gelest Inc.) in toluene for 72 hrs, sonicated with fresh toluene, rinsed with toluene, acetone and isopropanol and dried with nitrogen. Contact angle was ~ 70° for these substrates.

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 chloroform, 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 saturated with chloroform 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. Annealing at 200 °C for 15 min in N$_2$, with slow cooling (3° C/min) yielded the best OTFT performance, with lower temperatures giving lower μ, and higher temperatures resulting in film dewetting. Films destined for device fabrication had 40 nm gold contacts evaporated through a shadow mask (W/L = 20, L= 50 μm), while those for XRD studies did not.

We also fabricated control OTFT devices from un-purified PBTTT-C14, and obtained an average mobility of ~ 0.13 cm^{2}V^{-1}s^{-1}, which is in the normal range reported in the literature.

X-ray diffraction data was collected using a PANAlytical X'Pert-Pro X-ray diffractometer (ALMELO, The Netherlands) with a Cu anode and a K$_{\alpha_1}$ 1.54 Å wavelength. GIXD data was taken at the Stanford Synchrotron Radiation Laboratory 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).

OTFTs on PTS Substrates

We fabricated and characterized devices on SiO$_2$ surfaces but obtained marginal performance. Devices fabricated on phenyltrimethoxysilane (PTS) functionalized SiO$_2$ substrates showed low mobilities as displayed in **Fig. S4**. Devices on OTS substrates were used for all subsequent experiments.
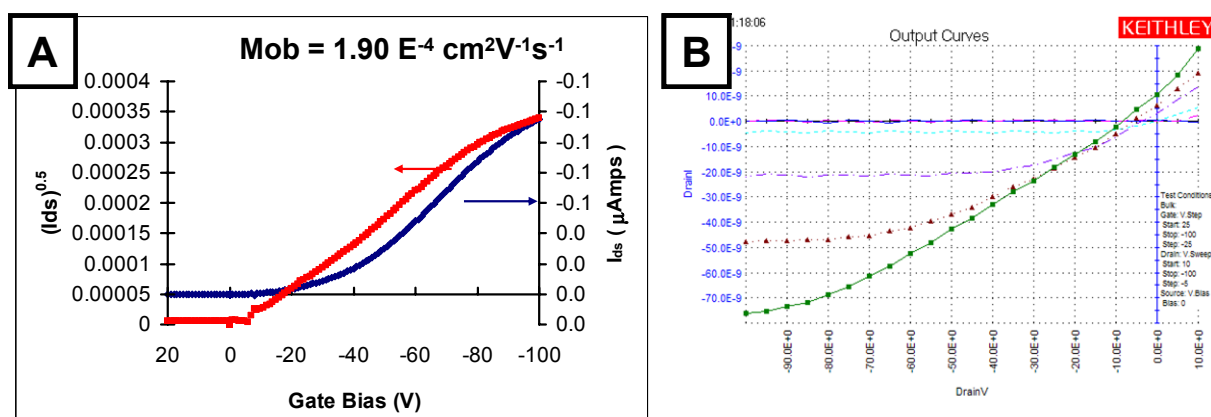
Figure S4. OTFT characteristics of a device fabricated with copolymer **1** on a PTS substrate.
Table S2. Variation of OTFT characteristics in air and N$_2$ environments Humidity is ~ 25% for all measurements.

Effect of Annealing Temperature and Time

In another experiment we evaluated the relative changes in transistor performance vs. the choice of annealing temperature and annealing time. The rational was that perhaps annealing times longer than 15 min, could allow the thin-films to restructure more fully. **Table S3** shows the results of a typical experimental run. In all cases the cooling rate was 3°C/min. We found that mobility sometimes increases with longer annealing times, but in all such cases the On/off ratio is severely degraded, and off current can increase by as much as 10^4. Annealing at 200° C for 15 min yielded the best combination of increased mobility and high On/off ratio.

Table S3. OTFT parameters after various thermal annealings.

| Copolymer	Annealed	Mob (Average) cm^2/Vs	RSD %	On/Off	Off Current (A)
1	No	1.7E-02	20%	2.9E+06	1.1E-11
1	180, 3 hrs	5.0E-02	15%	1.2E+06	8.0E-12
1	180, 9 hrs	3.9E-02	8%	2.0E+03	1.3E-08
1	200, 6 hrs	6.5E-02	17%	2.5E+03	7.6E-09
1	*200, 15 min*	*9.4E-02*	*10%*	*7.0E+06*	*2.2E-12*
4	No	3.2E-03	18%	1.9E+06	9.2E-12
4	180, 3 hrs	4.1E-02	11%	4.0E+04	5.2E-11
4	180, 9 hrs	6.2E-02	14%	7.8E+03	1.8E-09
4	200, 6 hrs	1.7E-02	23%	3.3E+03	5.6E-09
4	*200, 15 min*	*4.5E-02*	*6%*	*1.7E+06*	*1.5E-12*

As shown in **Fig. S7**, long annealing does not modify the characteristic shape of the I-V relations of our OTFTs measured in the glove box.
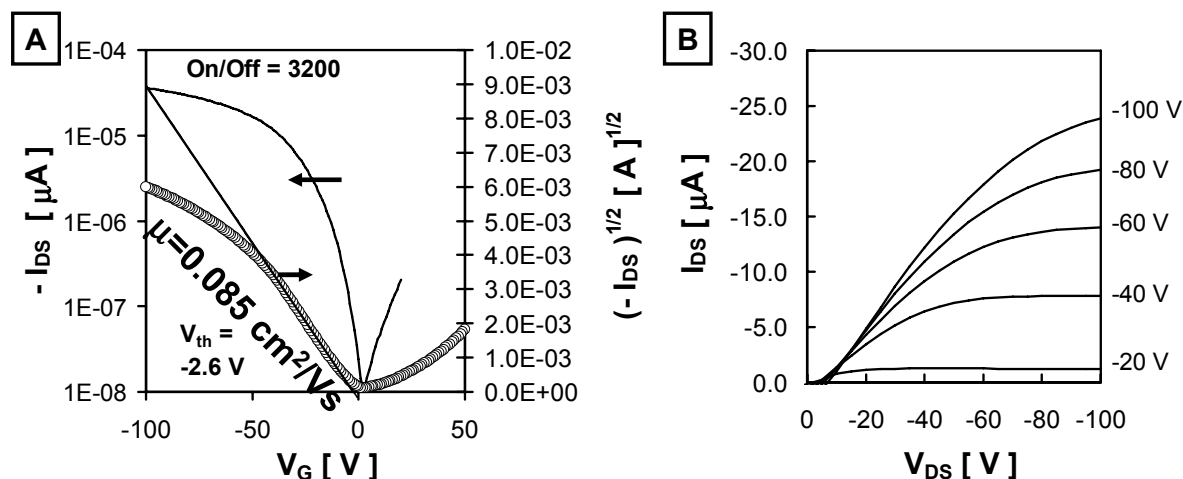
Figure S7. An OTFT fabricated on a thin film from copolymer 1, annealed to 200°C during 6 hrs in inert environment. Measurements taken also in dry N_2.

UV-Vis Absorption Spectroscopy of Copolymer Thin-films.

We drop-cast thin film from materials **1**, **4** and **5** from chloroform solutions onto quartz plates and measured their UV-Vis absorption using a CAREY 6000 Spectrophotometer. These spectra are shown in **Fig. S4.** All polymers show three absorption maxima ~ 320 nm, 445 nm and 650 nm, and the last two bands are separated by a deep minimum, suggestiong poor coupling between chomophores.
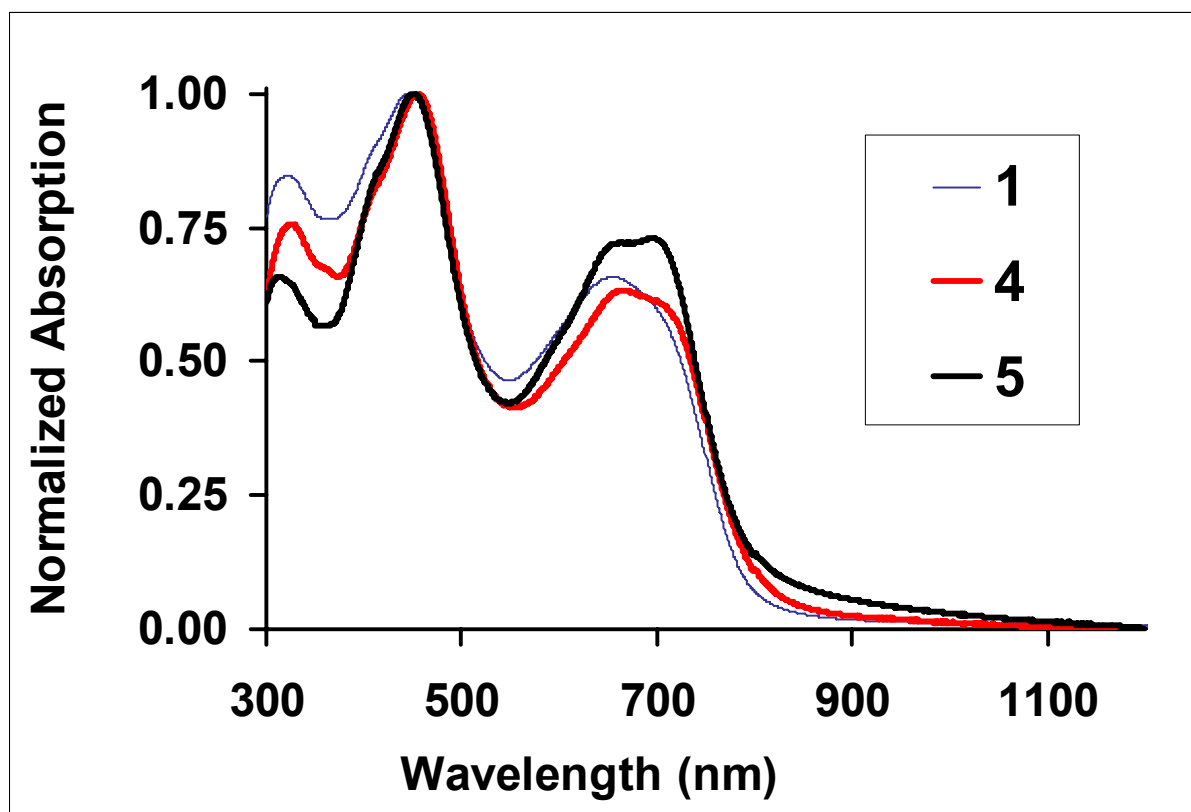
Figure S8. Normalized absorption spectra of thin-films of ACTP-F copolymers. **1** has three maxima at 321, 446, 650 nm, and an absorption onset of 799 nm; **4** shows maxima at 324, 454 and 662 nm, with an absorption onset of 806 nm; **5** has maxima at 312, 450, and 662 nm, and an absorption onset of 800 nm.

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 Keithly 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.