Molecular Design for Improved Photovoltaic Efficiency: Band Gap and Absorption Coefficient Engineering

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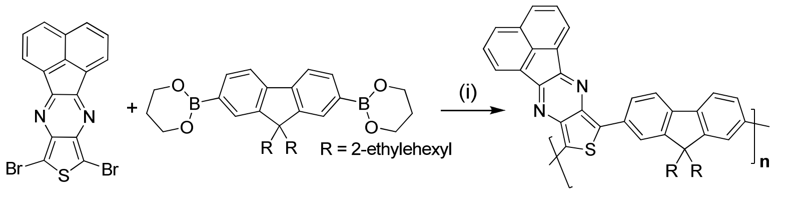
Supporting Information

Scheme S1.



ACT-FL

[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, 2 M aq. K_2CO_3, toluene, 90-95 ^oC, 5 days

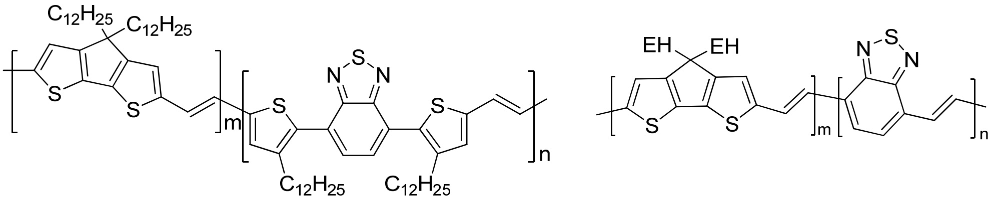


Chart S1. Vinylene linked 2,1,3-benzothiadiazole based copolymers.

General Experimental Methods. ^{1}H 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 weight was 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. 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 films for UV-vis in solid state were prepared by drop casting. Optical band-gaps were calculated from the edge of the visible-absorption bands in the film spectra. HOMOs of the polymers were estimated from the ionization potentials measured using photoelectron spectroscopy on the thin films.

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. 9,9-Di(2-ethylhexyl)fluorene-2,7-diboronic acid bis(1,3-propanediol) ester solution, tetrakis(triphenylphosphine)palladium (0), *N*-bromosuccinimide (NBS), Aliquot336, chlororbenzene, and *o*-dichlorobenzene were purchased from Aldrich or Alfa Aesar and used without further purification. Synthesis of 8,10-dibromoacenaphtho[1,2-*e*]thieno[3,4-*b*]pyrazine is reported elsewhere.[1]

Grazing incidence X-ray scattering (GIXS) measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) using beamline 11-3 with a photon wavelength of 0.09758 nm. Data was collected using a MAR345 image plate detector with a pixel size of 150 μm (2300 x 2300 pixels). The samples were ~20mm in the direction of the beampath, and the detector was located at a distance of 402.9 mm from the sample center. The incidence angle was chosen in the range of 0.10°-0.12° to optimize the signal-to-background ratio. The data was distortion-corrected (θ-dependent image distortion introduced by planar detector surface) before performing quantitative analysis. The overall resolution in the GIXD experiments, dominated by the sample size, was about 0.08 $Å^{-1}$

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). OTFT transfer and output characteristics were recorded in a dry nitrogen glovebox environment using a Keithley 4200 semiconductor parametric analyzer (Keithley Instruments, Cleveland OH).

Synthesis of ACT-FL:

0.624 mL of potassium carbonate solution (aq., 2M) was added to a mixture of 8,10-dibromoacenaphtho[1,2-*e*]thieno[3,4-*b*]pyrazine (100 mg, 0.208 mmol), 2,7-bis(trimethyleneborate)-9,9-bis(2-ethylhexyl)fluorene (116 mg, 0.208 mmol), tetrakis(triphenylphosphine)palladium (0) (10 mg), and Aliquat®336 (0.05 g) in 1 mL of chlorobenzene under argon. The reaction mixture was frozen and degassed under vacuum three times. Then the reaction mixture was heated to 90°C and stirred for 3 days. Crude polymer was precipitated in methanol and washed with hexane and acetone. The crude polymer was further purified by dissolving in ODCB with a palladium scavenger[2] followed stirring at 90 °C for 2 h. The polymer was reprecipitated in methanol and filtered and washed with methanol, acetone, and hexanes. **ACT-FL:** Yield = 79%; GPC (THF): M_w = 7283, M_n = 4700, PDI = 1.55; ^{1}H-NMR (300MHz, $CDCl_3$) δ 0.56-0.7 (m, 12H), 0.85-1.1 (br., 16H), 1.25 (m, 2H), 2.34 (br, 4H), 7.89 (br, 2H), 7.96 (br, 2H), 8.12 (br, 2H), 8.405 (br. 2H), 8.53 (br, 2H).

TGA and DSC of ACT-FL:

ACT-FL is thermally stable for >400 °C as indicated by thermogravimetric analysis (TGA). In differential scanning calorimetry (DSC), **ACT-FL** shows transition temperatures of 328 °C during heating and 315 °C during cooling, which were attributed to the melting point (T_m) and crystallization temperature (T_c), respectively (*Figure S4*).

Fabrication of thin film transistors:

Preparation of wafers: 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 deionized water and dried under a nitrogen stream. We modified the surface of these wafers with octadecyltrichlorosilane (OTS) to passivate charge traps in the oxide surface. 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°.

Device fabrication and testing: Due to its low M_w, the **ATC-FL** polymer was readily soluble in common organic solvents, but its film-forming properties on the highly hydrophobic OTS substrates were poor. Films for OTFTs were successfully formed by manual bar-coating of a concentrated drop of polymer solution in chloroform over OTS-treated SiO2/Si substrates inside a nitrogen glovebox. Films were not completely uniform and had thicknesses of the order of 30 – 50 nm. Films of **ACT-T-FL** polymer were prepared by drop-casting from toluene or chlorobenzene solutions onto OTS-treated substrates. All films were then dried on a hot plate at 80°C for 1 hr. After drying, selected films were further annealed at different temperatures. Annealing at 200 °C for 10 min in N_2, followed by slow cooling (3 °C/min) yielded the best OTFT performance. Films destined for device fabrication had 40 nm gold top-contacts evaporated through a shadow mask (W/L = 20, L= 50 μm), while those for GIXD studies did not.

Solar cell fabrication and testing:

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

30 nm layer of 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 and $PC_{[61]}BM$ solutions were spun at 900 rpm resulting in a film 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} torr. After electrode deposition, I-V 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.

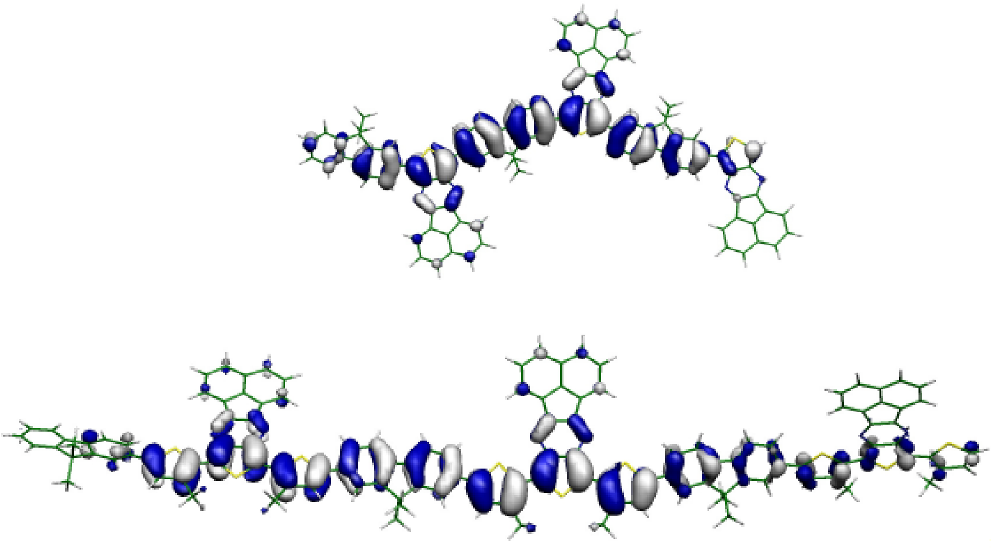


Figure S1. DFT-calculated HOMO of the geometry optimized structures of analogous trimers of **ACT-FL** and **ACT-T-FL**.

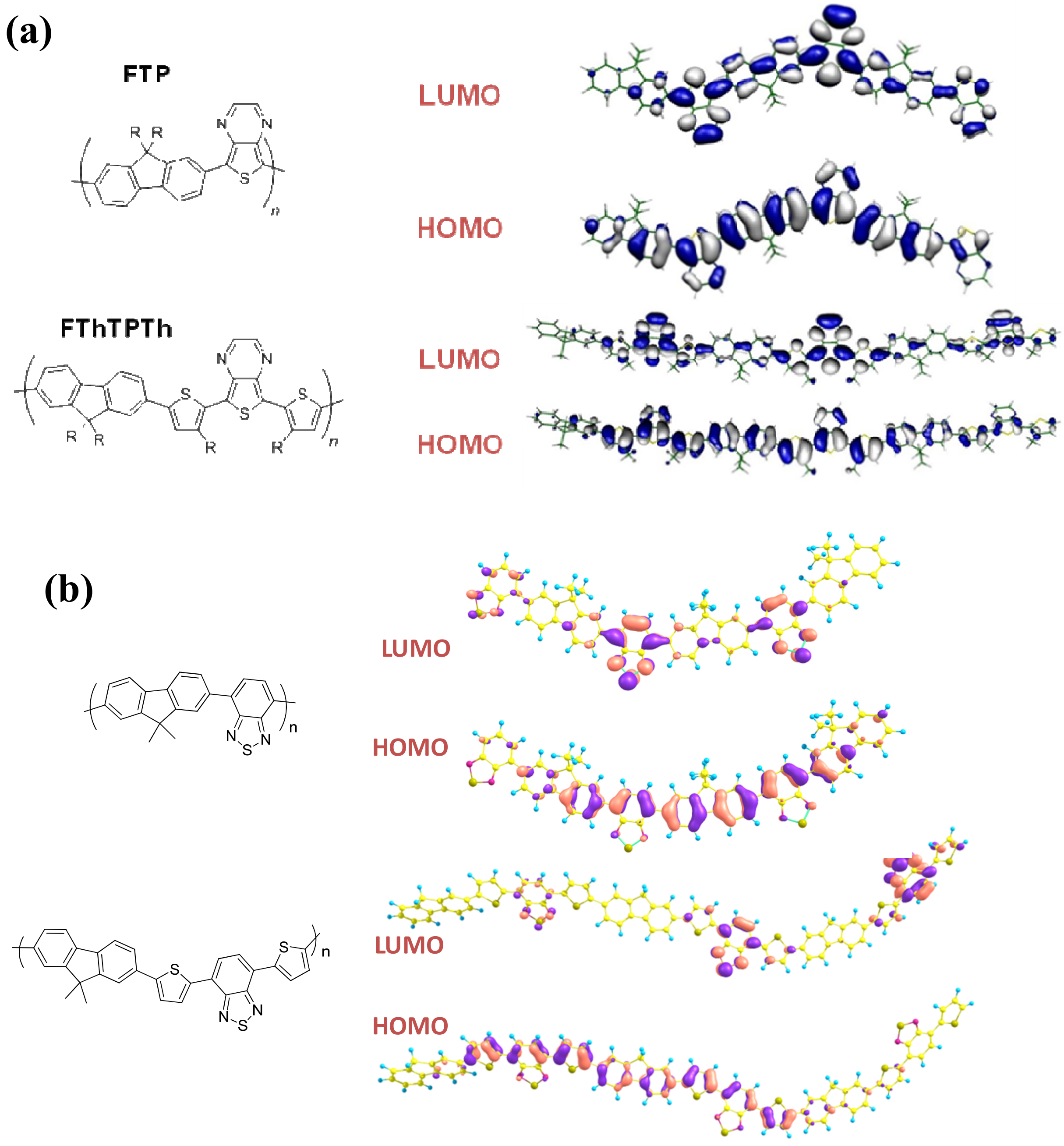


Figure S2. DFT-calculated HOMO and LUMO of the geometry optimized structures of (a) analogous trimers **ACT-FL** and **ACT-T-FL**, without the fused acenaphthyl unit; and (b) analogous trimers **ACT-FL** and **ACT-T-FL**, where thienopyrazine is replaced by 2,1,3-benzothiadiazole.

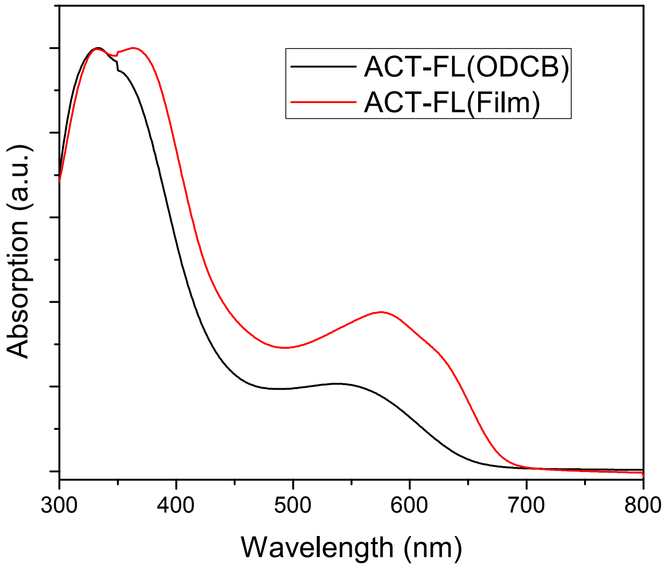


Figure S3. Absorption spectra of polymer **ACT-FL** in o-dichlorobenzene (black) and in thin film (red).

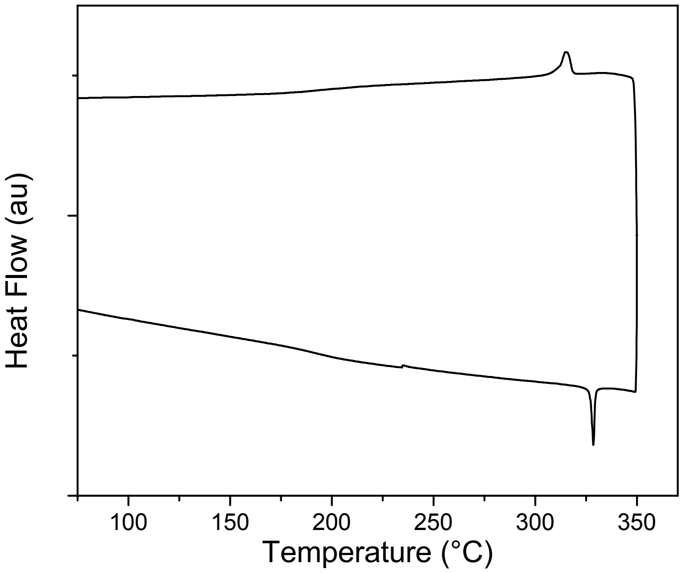


Figure S4. DSC curve of the co-polymer **ACT-FL** (2nd cycle). Transition temperatures of 328 °C during heating and 315 °C during cooling.

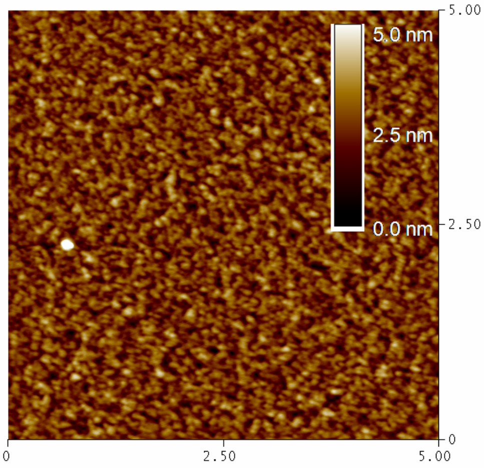


Figure S5. Tapping mode AFM image of annealed film of **ACT-FL** on bare Si substrate - annealed at ~200 °C (5µm×5 µm).

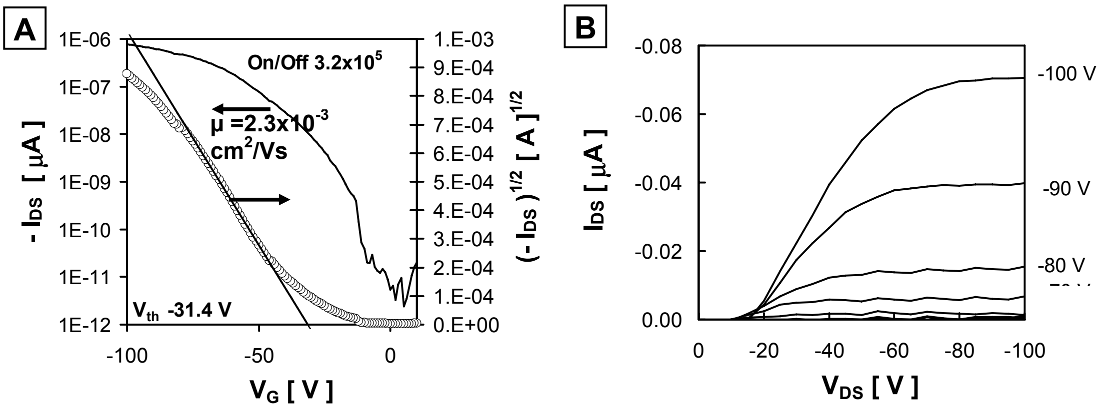


Figure S6. Representative I-V and output curves of *p*-type OTFTs of **ACT-FL** tested in an inert and dry atmosphere (glove box).

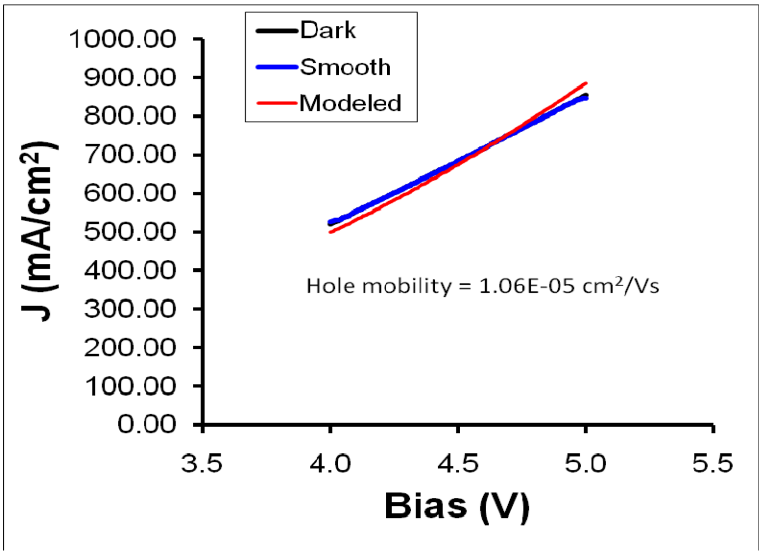


Figure S7. J-V plot for **ACT-FL** film (thickness = 50 nm) annealed at 200 °C and tested in an inert and dry atmosphere (glove box). Device structure - glass/ITO/PEDOT-PSS/polymer/Au.

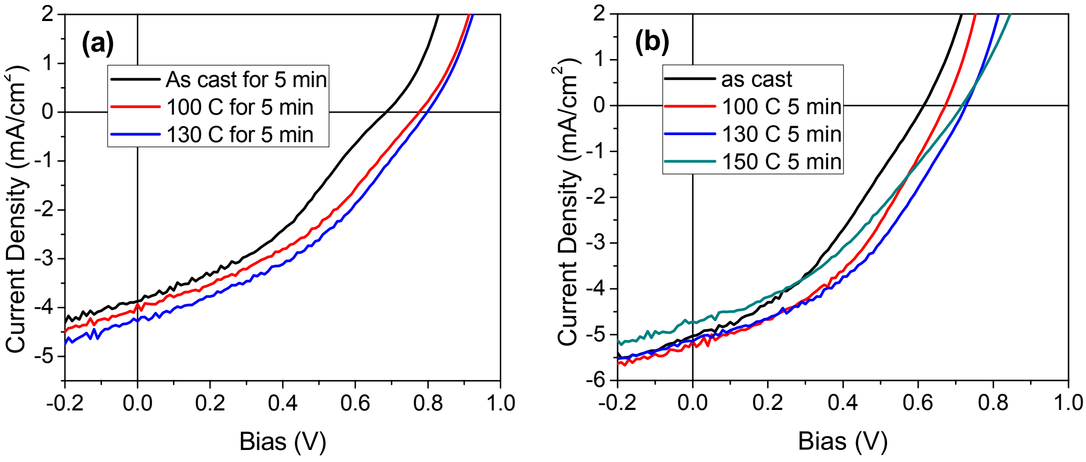


Figure S8. I-V characteristics under AM1.5 illumination for the solar cells fabricated from (a) 1:1 and (b) 1:4 blends of **ACT-FL** with $PC_{61}BM$ at different annealing temperatures.

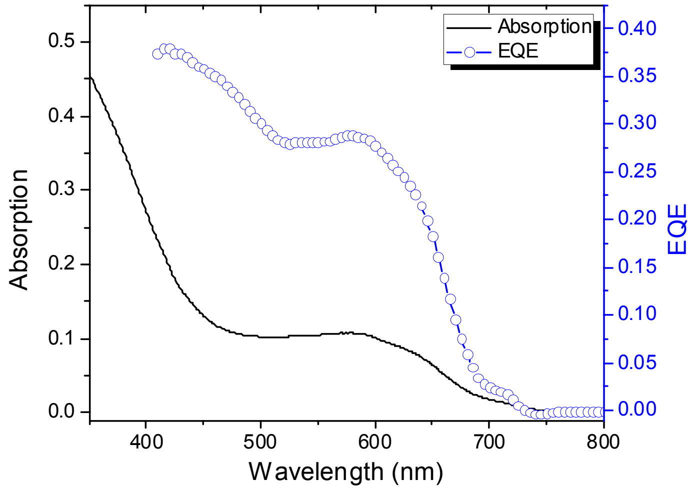


Figure S9. Absorption and EQE spectrum of a solar cell fabricated using blend of **ACT-FL** and $PC_{61}BM$ (1:4 wt. ratio) in the active layer.

Table S1. Photovoltaic properties of the Bulk Heterojunction Solar cells of **ACT-FL** at different blend ratio of $PC_{61}BM$ and different annealing temperatures.

Polymer	Blending ratio	Annealing temperature °C	J_{sc} mA/cm^2	V_{oc} V	FF	PCE %
ACT-FL	1:1	As cast	3.875	0.685	0.37	0.98
		100 °C	3.925	0.775	0.39	1.19
		130 °C	4.275	0.795	0.39	1.33
ACT-FL	1:4	As cast	5.035	0.615	0.37	1.15
		100 °C	5.141	0.675	0.42	1.46
		130 °C	5.141	0.725	0.42	1.57
		150 °C	4.717	0.715	0.37	1.25

References:

(1) Mondal, R.; Miyaki, N.; Becerril, H. A.; Norton, J. E.; Parmer, J.; Mayer, A. C.; Tang, M. L.; Brédas, J.-L.; McGehee, M. D.; Bao, Z. *Chem. Mater.* **2009**, *in press*.

(2) Nielsen, K. T.; Bechgaard, K.; Krebs, F. C. *Macromolecules* **2005**, *38*, 658-659.

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