

Electronic Supplementary Information

Improvement in Carrier Mobility and Photovoltaic Performance Through

Random Distribution of Segments of Linear and Branched Side Chains

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Experimental Part

Basic Characterization: The instrumentation and measurement conditions for basic characterization [WAXS (wide angle X-ray scattering), NMR (nuclear magnetic resonance), IR (infra red) and UV-visible spectroscopies, as well as elemental analysis, GPC (gel permeation chromatography), TGA (thermogravimetric analysis), DSC (differential scanning calorimetry), and mobility according to CELIV technique)] have been described elsewhere.^{1,2}

Organic Field Effect Transistors: The fabrication of the p-type **AnE-PVstat** Organic Field Effect Transistors (OFETs), with a staggered configuration (bottom gate, top drain and source), started with the deposition of the bottom gate electrode, Cr/Al, which was thermally evaporated in vacuum through a shadow mask on top of the glass substrate at a residual pressure below 10^{-6} mbar. The Cr and Al layer was 10 nm and 60 nm thick, respectively, and 2.5 mm wide. The thin Cr layer was deposited in order to increase the adhesion of the Al to the glass substrate. Afterwards, a layer of divinyltetramethyldisiloxane-bis(benzocyclobutene) (BCB) was deposited as gate dielectric by spin coating at 1500 revolutions per minute (rpm). The BCB was cured in a vacuum oven at 250 °C for 2 h following the standard procedure.³ The resulting BCB layer was 2 μm thick and had a capacitance of 1.18 nF/cm². The BCB was

used as received from Dow Chemicals. The polymer **AnE-PVstat**, dissolved in 1,2-dichlorobenzene with a concentration of 10 mg/ml, was deposited on top of the BCB as active layer of the transistor by spin coating at 600 rpm in a glove box with nitrogen atmosphere. The resulting **AnE-PVstat** layer was 80 nm thick. The fabrication of the transistor ends with the vacuum thermal evaporation, through a shadow mask of 100 nm thick top Au drain and source contacts at a residual pressure below 10^{-6} mbar. The obtained transistor channel is 80 μm long and 2 mm wide. The electrical characterization of the OFETs was carried out at room temperature and in nitrogen atmosphere by using an Agilent E5273A 2 Channel (High Power, Medium Power) Source/Monitor Unit.

Photovoltaic studies: For the fabrication of bulk heterojunction type solar cells, solutions were prepared with three mixture ratios (1:1, 1:2 and 1:3) of **AnE-PVstat** to the acceptor [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) in chlorobenzene with a concentration of (30mg **AnE-PVstat**: PCBM)/ml stirred overnight. The indium tin oxide (ITO) coated glass substrate was first cleaned by ultra-sonication successively with glass cleaning detergent helmanex, acetone, isopropanol and deionized water and dried by purging with air. Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) (Baytron PH) stirred overnight and filtered was spin coated from aqueous solution on top of ITO with 3000 rpm to get a film of 50-55 nm thickness and dried overnight in open air. The **AnE-PVstat**: PCBM solution was then filtered and spin-coated on top of PEDOT/PSS film with 1000 rpm. Then the sample was kept in the glove box to dry for 24 h and the top electrode aluminum metal (100 nm) deposition was done by thermal evaporation in vacuum of about 5×10^{-6} bar. Current-voltage (I-V) characteristics of the devices were measured using a Keithley 236 source measurement unit under 100 mWcm^{-2} AM 1.5 white light illumination of the solar cell. Incident photon to current efficiency (IPCE) or external quantum efficiency (EQE) measurements were taken using a fiber optical light source from 90 W Xenon lamp, which is connected to a ACTON Spectra Pro150 monochromator and EG & G 7260 DSP Lock in amplifier to measure the current. Both I-V and IPCE measurements were done before and after annealing of the solar cells at 110 °C for 5 minutes in the same glove box. The active layer of solar cells consists of **AnE-PVstat**: PCBM with thickness of ~190 nm for 1:1 and ~245 nm for both 1:2 and 1:3 ratios. PEDOT: PSS layer is about ~50 nm.

Materials: The various starting chemicals were purchased from commercial suppliers (Sigma-Aldrich-Fluka) and were used without further purification unless specified. Solvents were dried and distilled according to standard procedures and stored under argon. If not otherwise

specified, solvents or solutions were degassed by bubbling with nitrogen for 1 h prior to use. The syntheses of polymers **AnE-PVaa**, **-ad**, **-ab**, **-ba**, **-bb** have been described elsewhere.¹

Poly-{1,4-[2,5-dioctyloxy-or-di(2-ethylhexyloxy)]phenylene-ethynylene-9,10-anthracenylene-ethynylene-1,4-[2,5-dioctyloxy-or-di(2-ethylhexyloxy)]phenylene-vinylene-1,4-[2,5-dioctyloxy-or-di(2-ethylhexyloxy)]phenylene-vinylene} AnE-PVstat

9,10-Bis{[2,5-di(2-ethylhexyloxy)-4-formyl]phenyl}-ethynyl}anthracene¹ (**1a**) (100 mg, 0.1055 mmol) and 9,10-Bis{[2,5-di(2-ethylhexyloxy)-4-formyl]phenyl}-ethynyl}anthracene¹ (**1b**) (100 g, 0.1055 mmol), 2,5-dioctyloxy-*p*-xylylene-bis(diethylphosphonate)¹ (**2a**) (67 mg, 0.1055 mmol), 2,5-di(2-ethyl)-hexyloxy-*p*-xylylene-bis(diethylphosphonate)¹ (**2b**) (67 mg, 0.1055 mmol) were dissolved in dry toluene (20 mL). The mixture was heated under reflux and an excess potassium-*tert*-butoxide (96 mg, 0.856 mmol) was added in small portions. After 1.5 h reaction time, more toluene was added and the reaction was quenched after pouring 5% aqueous HCl (20 mL) into the mixture. The organic phase was separated and washed six times with deionized water until the aqueous phase became nearly neutral (pH = 6-7). The remaining water was removed by heating using a Dean-Stark apparatus. The resulting toluene solution was filtered and evaporated under vacuum to a small rest, which was subsequently precipitated into cold methanol. The polymer was filtered off, dried and extracted for 1.5 h with a 1:1 mixture of methanol:diethylether. Yield: 240 mg (89.24%). GPC (THF as eluent, polystyrene standards): UV detector: $M_n = 27,500$ g/mol, $M_w = 56,900$ g/mol, $M_z = 97,000$ g/mol, $M_p = 49,700$ g/mol. PDI = 2.0, $P_n = 22$; IR detector: $M_n = 28,100$ g/mol, $M_w = 58,000$ g/mol, $M_z = 104,400$ g/mol, $M_p = 50,700$ g/mol. PDI = 2.0, $P_n = 22$. ¹H NMR (CDCl₃, 200 MHz): δ /ppm = 8.90→8.70, 7.58→7.53 and 6.86→6.80 (18H, arylene and vinylene H's); 4.47→3.62 (12H, -CH₂O-); 2.20→0.79 (90H, CH₃(CH₂)₆- and CH₃(CH₂)₃CH(CH₂CH₃)-). FTIR: 3058 (w, C_{aryl}-H), 2955, 2923 and 2856 (s, -CH₂- and -CH₃), 2185 (w, disubst.-C≡C-), 1620 and 1598 (w, aryl-C=C-), 1200 (vs, C_{phenyl}-OR), 968 (s, trans -CH=CH-) cm⁻¹. Anal. Calcd for (C₈₈H₁₂₀O₆)_n (1273.91)_n: C, 82.97; H, 9.49. Found: C, 81.56; H, 9.86.

1. Egbe, D. A. M.; Türk, S.; Rathgeber, S.; Kühnlenz, F.; Jadhav, R.; Wild, A.; Birckner, E.; Adam, G.; Pivrikas, A.; Cimrova, V.; Knör, G.; Sariciftci, N. S.; Hoppe, H. *Macromolecules* **2010**, *43*, 1261.
2. Rathgeber, S.; Bastos de Toledo, D.; Birckner, E.; Hoppe, H.; Egbe, D. A. M. *Macromolecules* **2010**, *43*, 306.

3. CYCLOTENE* 3000 Series Advanced Electronic Resins. Published Literature. Dow Chemicals, February 2005.

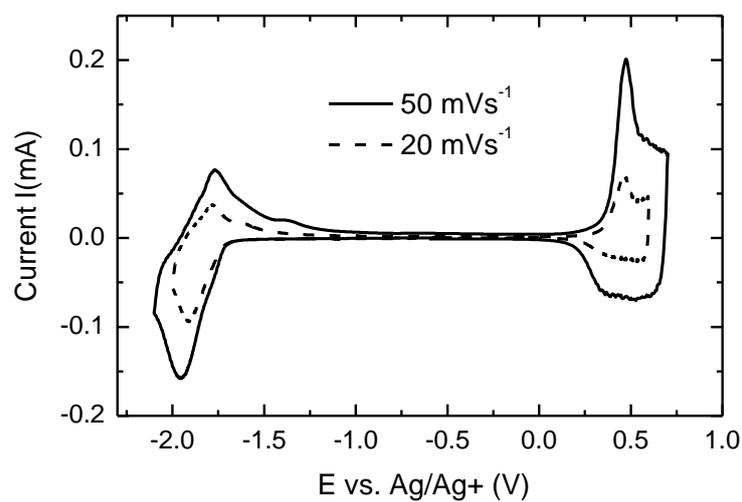


Figure S1. Representative cyclic voltammogram of **AnE-PVstat** film coated on Pt wire recorded at the scan rates 20 and 50 mV/s.

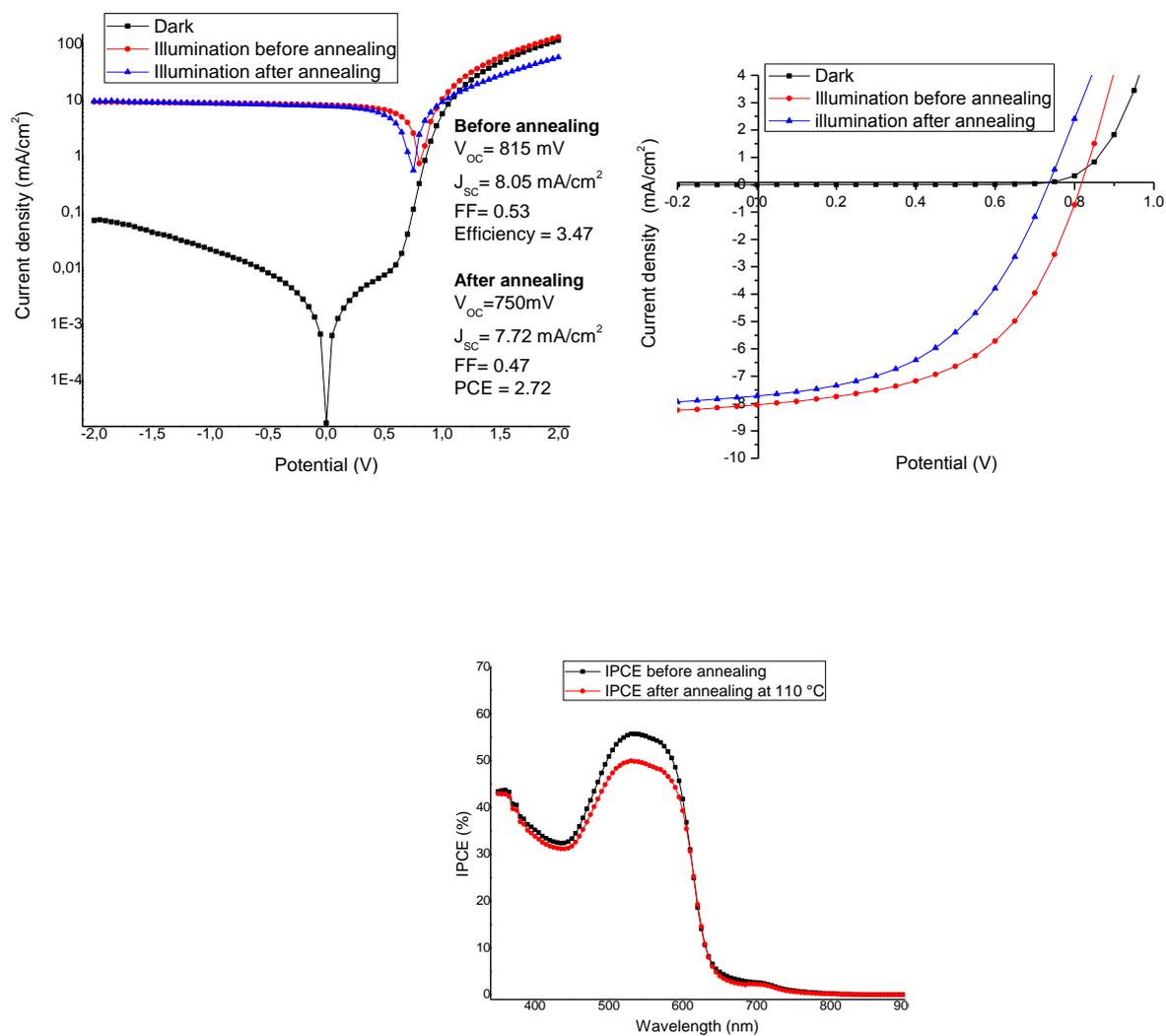


Figure S2: IV-curve of AnE-PVstat:PCBM (1:1) blend solar cell and the corresponding IPCE.

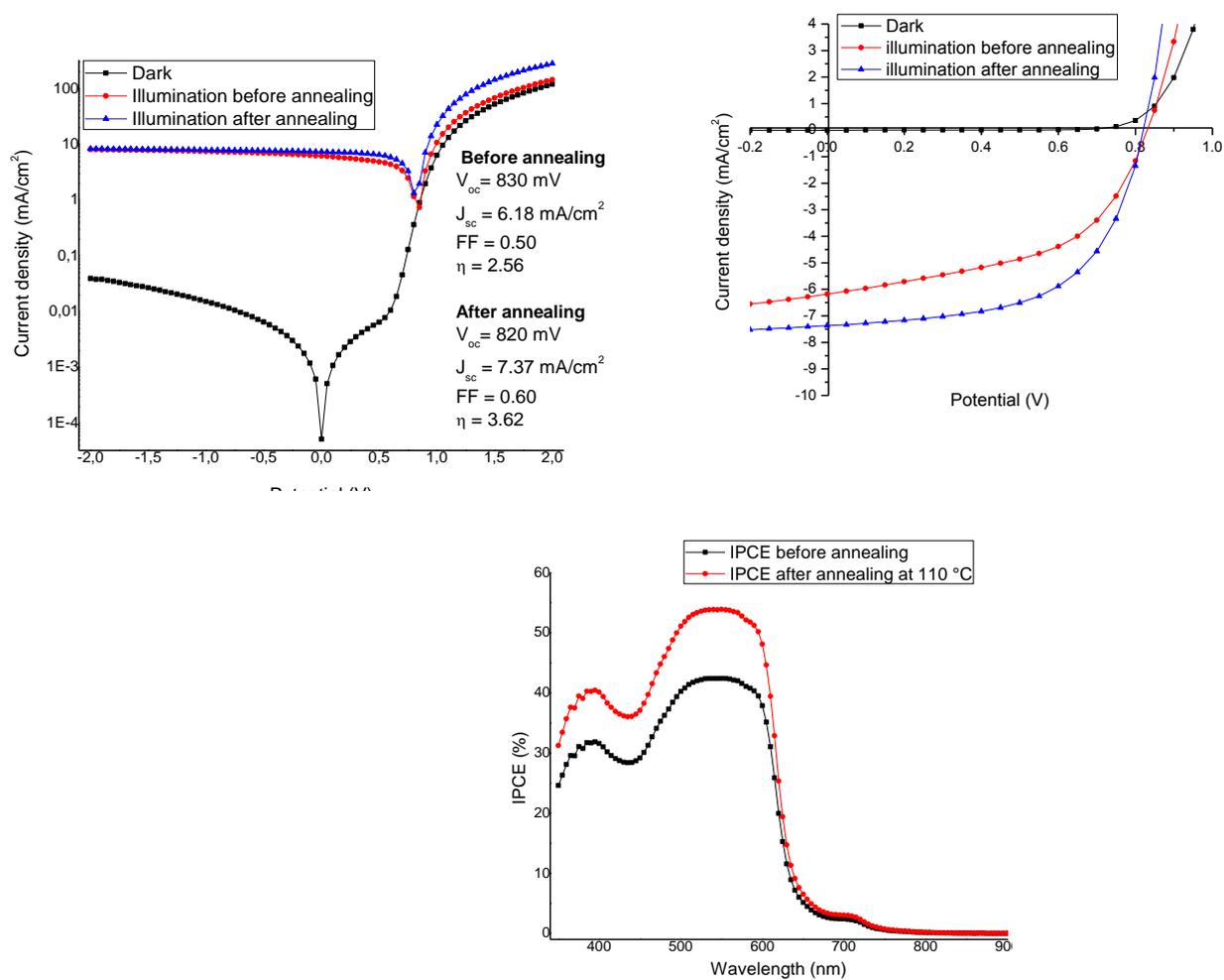


Figure S3: IV-curve of AnE-PVstat:PCBM (1:3) blend solar cell and the corresponding IPCE.

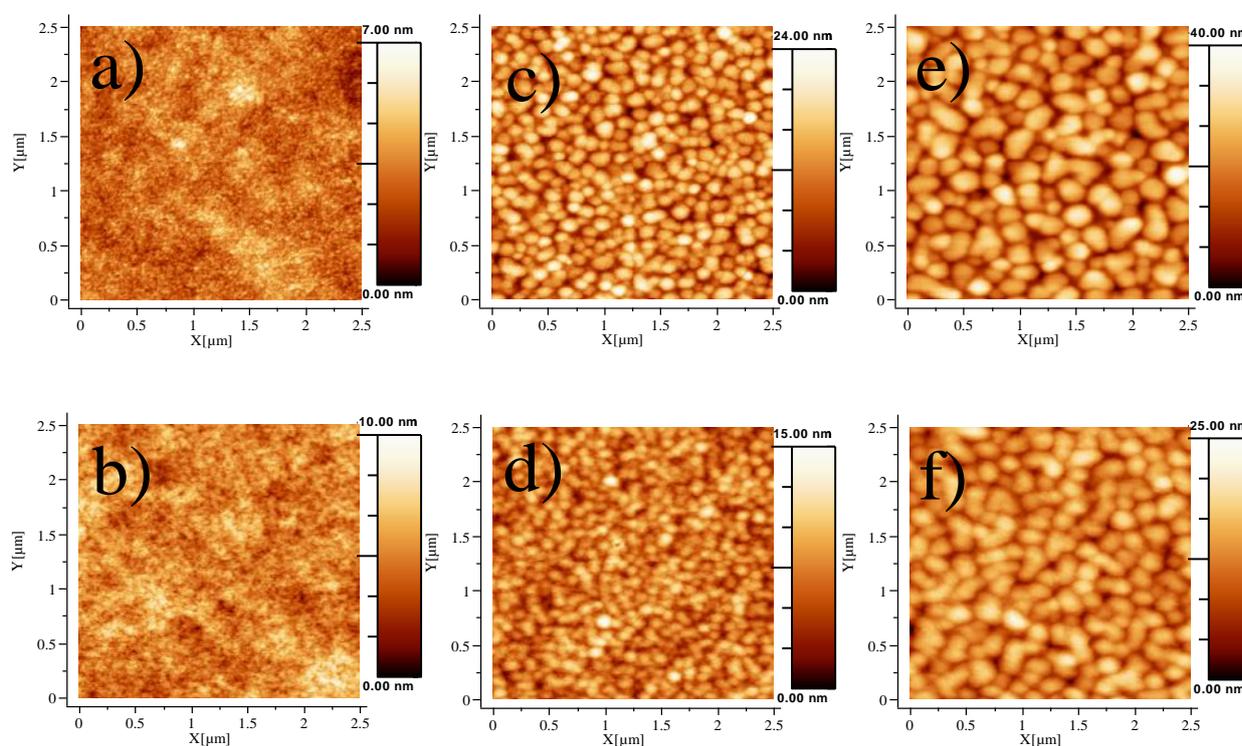


Figure S4. AFM images of **AnE-PVstat:PCBM** films for three different blend ratios, before and after annealing: a) 1:1 ratio before annealing, b) 1:1 ratio after annealing, c) 1:2 ratio before annealing, d) 1:2 ratio after annealing, e) 1:3 ratio before annealing, f) 1:3 ratio after annealing.

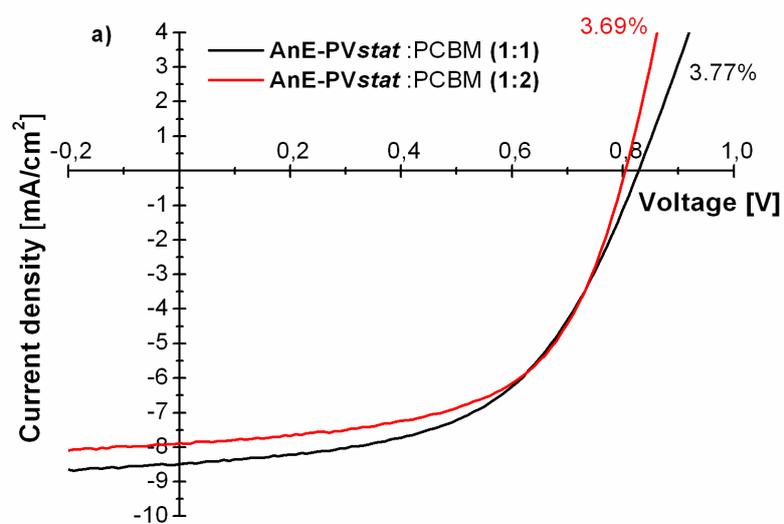


Figure S5. IV Curves of the best solar cells from 1:1 and 1:2 **AnE-PVstat:PCBM** obtained from thinner active layers under identical experimental conditions as in ref. 1.