Improving solar cell morphology with stepwise self-assembly

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Supporting Information

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1. General

All chemicals were purchased from commercial sources (Sigma Aldrich, Acros and TCI) and used as received. Anhydrous solvents for synthesis are distilled from a VAC solvent purifier from Vacuum Atmospheres Company. Chlorobenzene and toluene for device fabrication are purchased from Sigma Aldrich and stored in a N_2 glovebox. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. All NMR spectra were taken with compound concentrations of 1-5 mM in CDCl3. ^{1}H-NMR and ^{13}C-NMR were recorded on a Varian 500 MHz or Bruker 500 MHz NMR spectrometer at 295 K. The molecular weight was analyzed by using a PE Voyager DE-Pro MALDI-TOF-MS instrument.

2. Synthesis

Synthesis of (5-bromo-thiophene-2-yl)- methanol (2)

5-bromo-2-thiophencarboxaldehyde **1** (6.5 g, 34 mmol) was dissolved in anhydrous THF (40 ml) in an oven-dried two-necked round-bottom flask with a stir bar. The solution was cooled down to 0 °C and a 1M in THF solution of lithium aluminum hydride (8.5 ml, 8.5 mmol) was added dropwise for 10 minutes. After 12 hours the reaction was quenched with 2 ml of NaOH $2M_{(aq)}$ and extracted with between dichloromethane and water. The organic layer was collected and dried over MgSO4. The solvent was evaporated under vacuum and the crude was passed through a silica column to eliminate rests of starting material using dichloromethane as the eluent. Compound **2** was obtained as a yellow oil in 86% yield (5.7 g, 0.0295mmol). ^{1}H-RMN (500 MHz, $CDCl_3$): δ 6.89 (d, 1H), 6.69 (d, 1H), 4.64 (d, 2H), 3.30 (s_{broad}, OH).

Synthesis of (5-tributylstannyl-thiophene-2-yl)-methanol (3)

Compound 2 (5 g, 26 mmol) was dissolved in anhydrous THF (40 ml) in an oven-dried two-necked round-bottom flask with a stir bar and rigorously degassed with nitrogen flow during 10 minutes. The solution was cooled down to 0 °C and NaH in mineral oil (60%) (1.14 g, 28 mmol) was added. The reaction was allowed to run for one hour. After this time the reaction was cooled down in an acetone/dry ice bath to -78 °C under nitrogen. *n*-Butyllithium (2.5 M in hexanes, 12 ml, 31mmol) was introduced dropwise by a syringe in a period of 10 minutes into the flask. The reaction was stirred for 3 more hours at -78 °C. Tributylstannyl chloride (17 ml, 65 mmol) was added with a syringe to the flask and the acetone/dry ice bath was removed to allow the reaction to reach room temperature. After 12 hours, the reaction mixture was transferred to a round- bottom flask and the solvent was evaporated under vacuum. The crude was dissolved in hexanes and passed through a short silica gel column. The filtrate was placed under reduce pressure to eliminate the solvent. Compound **3** was obtained as a dark yellow oil in 80 % yield (8.04 g, 20 mmol). ^{1}H-RMN (500 MHz, $CDCl_3$): δ 6.90 (d, 2H), 6.73 (d, 2H), 4.69 (d, 4H), 1.63 (m, 6H), 1.36–1.32 (m, 12H), 0.93 (q, 9H). ^{13}C-RMN (125 MHz, $CDCl_3$): δ 144.02, 126.89, 125.65, 125.50, 60.06, 27.83, 27.16, 13.70.

Synthesis of 5

Compounds **4**[1] (11 mg, 0.034 mmol) and **3** (30 mg, 0.075 mmol) are placed in a round-bottom flask with a stir bar and dissolved in anhydrous dichloromethane (5 ml). N-ethyl-N'-(dimethylaminopropyl)carbodiimide (EDC, 43 mg, 0.22 mmol) and 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS, 67 mg, 0.22 mmol) were subsequently added to the reaction mixture. The reaction was stirred for 48 hours and after completion the reaction crude was extracted between dichloromethane and $NaHCO_3$(aq) (50 ml x 1), water (50 ml x 2) and brine (50 ml x 1). The organic phase was dried over $MgSO_4$. Compound **5** was obtained after silica gel column chromatography (dichloromethane, dichloromethane/methanol 10:1) as a colorless oil in 54% yield (20 mg, 0.018 mmol). ^{1}H-RMN (500 MHz, $CDCl_3$): δ 6.90 (d, 2H), 6.73 (d, 2H), 5.35-5.28 (dd, 4H), 3.65 (s_{broad}, 2H), 2.09-.94 (m, 2H), 2.72-2.71 (m, 4H), 2.48-2.42 (m 4H), 1.80-1.74 (m, 4H), 1.28-1.19 (s, 2H), 1.67-1.50 (m, 12H), 1.38-1.29 (m, 12H), 1.13-1.08 (t, 12H), 1.01-0.83 (q, 18H). ^{13}C-RMN (125 MHz, $CDCl_3$): 172.25, 172.12, 143.08, 135.25, 129.45, 128.15, 126.86, 60.67, 53.69, 32.26, 30.78, 29.59, 28.77, 27.94, 27.34, 26.99, 24.86, 13.73, 10.89. δ ESI (m/z): $(M+ Na)^+$ Calculated for $C_{48}H_{82}N_2O_6S_2Sn_2$: 1086.3658; found: 1110.872.

Synthesis of LDM

Compound **6**[2] (37 mg, 0.06 mmol) and 2-tributylstannyl-thiophene (25 mg, 0.06 mmol) are placed in an oven-dried two-neck round-bottom flask with a stir bar and dissolved in anhydrous DMF (2 ml). The reaction is rigorously degassed under nitrogen flow for 10 minutes and heated to 80 °C. $Pd(PPh_3)_4$ (70.0061 mg, mmol) is added. After 12 hours the reaction is cooled down and passed through a short column of celite to remove Pd(0). The column was washed with dichloromethane several times. The solvent was evaporated under reduced pressure and the product was purified by silica gel column chromatography (hexanes/dichloromethane 8:2). DPP-Control was obtained as a purple solid in 55% yield (20 mg, 0.033 mmol). ^{1}H-RMN (500 MHz, $CDCl_3$): δ 8.92 (d, 1H), 8.87 (d, 1H), 7.62 (d, 1H), 7.33-7.31 (m, 3H), 7.27 (d, 1H), 7.08 (t, 1H), 4.05-4.01 (m, 4H), 1.98-1.82 (m, 2H), 1.39-1.25 (m, 16 H), 0.92-0.84 (m, 12H). ^{13}C-RMN (125 MHz, $CDCl_3$): δ 161.81, 161.65, 142.85, 140.07, 139.94, 136.81, 136.19, 135.22, 130.48, 129.90, 128.46, 128.31, 128.0, 126.33, 125.21, 124.81, 108.12, 108.09, 45.91, 39.24, 39.08, 30.32, 30.19, 28.52, 28.35, 23.64, 23.52, 23. 13, 14.12, 10.57. ESI (m/z): $(M + H)^+$ Calculated for $C_{34}H_{42}N_2O_2S_3$: 606.9045; found: 608.103.

Synthesis of DPPHP

Compounds **5** (52 mg, 0.047mmol) and **6**[2] (72mg, 0.12 mmol) are placed in an oven-dried two-neck round-bottom flask with a stir bar and dissolved in anhydrous DMF (ml). The reaction mixture is rigorously degassed under nitrogen flow for 10 minutes and heated to 80 °C. $Pd(PPh_3)_4$ (11 mg, 20%) is added. After 12 hours the reaction is cooled down and passed through a short column of celite to remove Pd(0). The column was washed with dichloromethane several times. The solvent was evaporated under reduced pressure and the product was purified by silica gel column chromatography (hexanes/dichloromethane 8:2). **DPPHP** was obtained as a purple solid in 25% yield (17 mg, 0.011 mmol). ^{1}H-RMN (CDCl3): δ 8.92 (d, 2H), 8.86 (d, 2H), 7.64 (d, 2H), 7.24 (d, 2H), 7.00-7.02 (m, 4H), 6.96 (t, 2H), 6.20 (1H, NH), 6. 07 (1H, NH), 5.30 (d, 2H), 5.23 (d, 2H), 4.08 (m, 8H), 2,73-2,62 (m, 4H), 2.49-2.42 (m, 4H), 2.03 (m, 4H), 1.73 (s, 4H), 1.35-1.31 (m, 32 H), 0.93–0.85 (m, 24H). ^{13}C-RMN (125 MHz,$CDCl_3$):δ 164.29, 161.11, 140.25, 138.43, 135.42, 135.12, 131.43, 130.88, 129.40, 128.48, 118.89, 107.83, 107.4, 53.64, 42.21, 32.40, 31.95, 26.70, 22.40, 14.10, 10.57. ESI (m/z): $(M + H)^+$ Calculated for $C_{84}H_{106}N_6O_{10}S_6$: 1552.16; found: 1553.399

3. UV-Visible Spectroscopy (UV-Vis)

UV-Vis spectra in solution were collected on a PerkinElmer Lambda 1050 spectrophotometer using a quartz cell of 0.1 cm path length. Transmission spectroscopy was collected in the same instrument using a mica slide as a background.

4. Fluorescence Spectroscopy

Fluorescence spectra were performed on an ISS PC photon counting fluorometre using a quartz cell of 1 cm path length, in which all emission spectra were collected at a 90° angle at room temperature.

5. Atomic Force Microscopy

AFM characterization was performed using a Bruker Dimension ICON atomic force microscope (Bruker Co.) at ambient conditions. Tapping mode was utilized with single-beam silicon cantilevers with a nominal oscillation frequency of 300 kHz.

6. Cryo Transmission Electron Microscopy

CryoTEM was performed using a JEOL 1230 transmission electron microscope operating at 100kV fitted with a LaB_6 filament. A 5μL drop of the sample in toluene was deposited on a 300 mesh copper grid with a lacey carbon support (Electron Microscopy Sciences), blotted with filter paper, and plunge frozen using liquid nitrogen as a cryogen with a Vitrobot Mark IV (FEI) vitrification robot at ambient temperature and humidity. The samples were placed into a Gatan 626 cryo-holder using a cryo-transfer stage and imaged using a Gatan 831 CCD camera.

7. Electrochemical measurements

Electrochemical measurements were done by cyclic voltammetry on a three electrode setup (EG&G Princeton Applied Research potentiostat model 263A). **DPPHP** was drop cast from chlorobenzene solution (3.2×10^{-3} M) onto the working electrode. The film was immersed into anhydrous chlorobenzene after degassing the solvent and scanned at 100 mV/s using tetrabutylammonium hexafluorophosphate (NBu_4PF_6) as the electrolite. A gold working electrode, a silver pseudoreference electrode and a platinum counterelectrode were used. Ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as the internal standard and an absolute energy level of -4.8 vs vacuum was assigned. Electrochemical potential is reported vs SCE, which has an energy of -4.44 eV vs vacuum. The HOMO level of **DPPHP** was determined by equation 1. The LUMO level was calculated by equation 2.

$$E_{HOMO} = -(E_{ox}^{onset} + 4.80)\ (eV)\ \textbf{(eq 1)}$$

$$E_{LUMO} = E_g^{opt} + E_{HOMO}\ (eV)\ \textbf{(eq 2)}$$

8. Device Fabrication

Experimental conditions such as film thickness, DPPHP and DPP-Control concentration and solvent composition were optimized. Prepatterned indium-doped tin oxide (ITO) on glass was used as the transparent bottom electrode. The ITO was scrubbed with sopay water and cleaned by ultrasonicating sequentially in hexanes, soapy water, water, and a 1:1:1 solution of acetone/methanol/2-propanol. The electrode was then blown dry in a N_2 stream. The ITO surface was cleaned by UV-ozone treatment, and thin film of PEDOT:PSS (Clevios P VP Al 4083) was immediately spin-cast on top. The PEDOT:PSS film was dried at 120 °C for 20 minutes and transferred into a N_2 glovebox (O_2 and H_2O < 0.1 ppm). Bulk heterojunction photovoltaic devices were fabricated from blends of **DPPHP** or **DPP-Control** and phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$). Solutions of 7 mg/mL of **DPPHP** or **DPP-Control** where prepared according to the stepwise self-assembly protocol in either chlorobenzene or toluene and solutions of 27 mg/mL **$PC_{71}BM$** (filtered through 0.22 μm porous polytetrafluoroethylene filters) were prepared in chlorobenzene. The blends were prepared adding the **$PC_{71}BM$** solution to a previously assembled solution of **DPPHP** or **LDM** and mixing for periods of time between 0.5 to 5 minutes.

Films were cast by spin-coating at various speeds in the glovebox for 60 s. Total organic layer thickness ranged from 70-80 nm as determined by profilometry.

Devices were completed by thermally evaporating 6 Å of LiF then 100 nm of Al through a shadow mask at 1 x 10^{-6} mbar to yield devices of 4 mm^2 in area and sealed with a UV-curable epoxy.

9. Device Measurements

Two-terminal measurements were performed using a Keithley 2400 source meter. Photovoltaic measurements were done while the devices were illuminated by an Oriel Xe solar simulator equipped with and Oriel 130 monochromator. Filters were used to cut off grating overtones. The solar spectrum was simulated using an AM 1.5 filter with 100 mW/cm2 power density. A calibrated silicon reference solar cell with a KG5 filter certified by the National Renewable Energy Laboratory was used to confirm the measurement conditions.

10. Space-Charge-Limited-Current (SCLC) Measurements

SCLS experiments were used to measure the hole mobility of 40:60 blends of **DPPHP/$PC_{71}BM$** and **LDM/ $PC_{71}BM$** in a solar cell configuration. These devices were fabricated under identical conditions to the reported solar cells except that the LiF/Al was replaced with Au in order to suppress electron injection. Hole mobility were estimated using the data showed in Figure S* and theory reported by V. D. Mihailetchi et al.[3] V_{RS} = Voltage Drop across the ITO series resistance and V_{BI} = Built-in voltage.

11. Supporting Figures

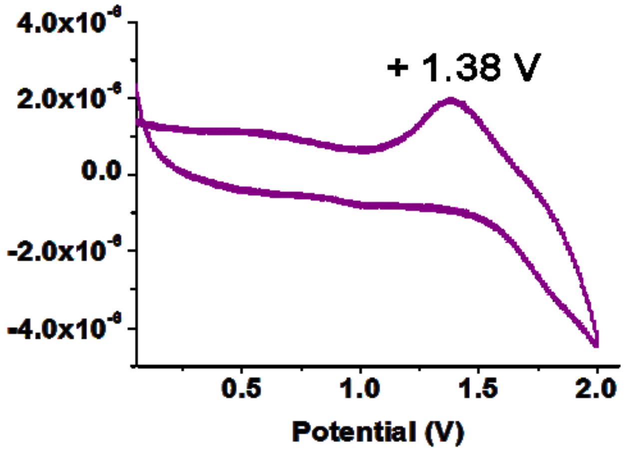

Fig. S1: Cyclic voltammogram of the oxidation of **DPPHP**.

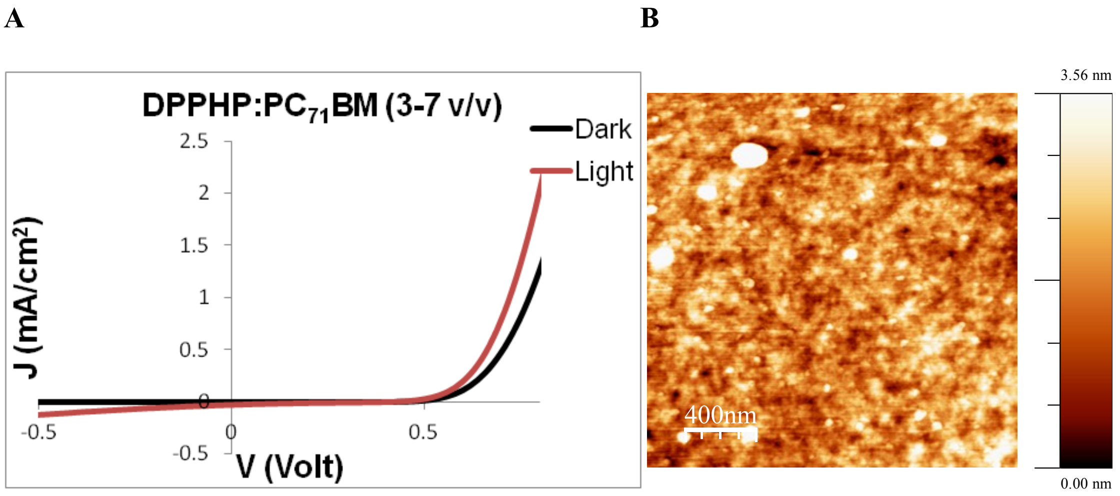

Fig. S2: JV curve of devices fabricated by in situ self-assembly (**A**). Morphology of the active layer of devices fabricated by in single step self-assembly (**B**).

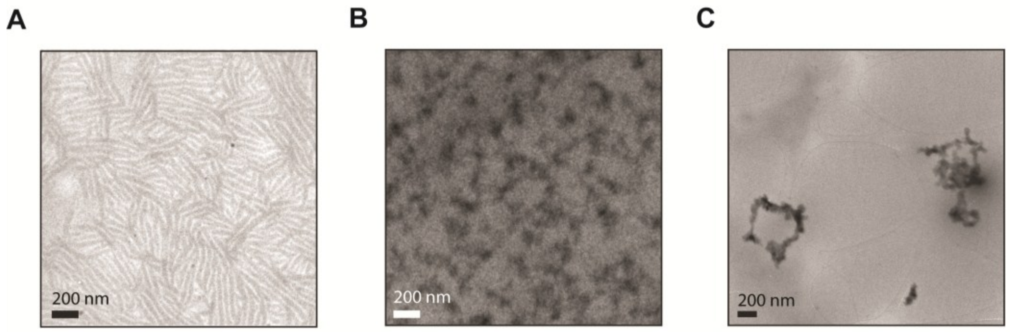

Fig. S3: CryoTEM images of **DPPHP** solution (**A**). **DPPHP** + **PC$_{71}$BM** solution (**B**). **PC$_{71}$BM**. [**DPPHP**] = 7 mg/ml. [**PC$_{71}$BM**] = 27 mg/ml (**C**).

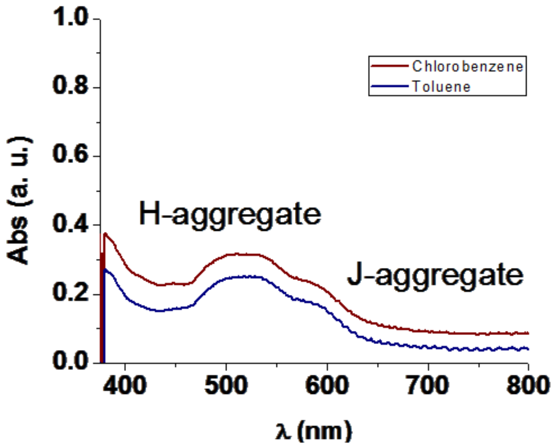

Fig. S4: Absorption spectra of **DPPHP** thin films spin cast on mica at 1500 rpm in toluene and chlorobenzene. [**DPPHP**] = 4.5 x 10^{-3} M.

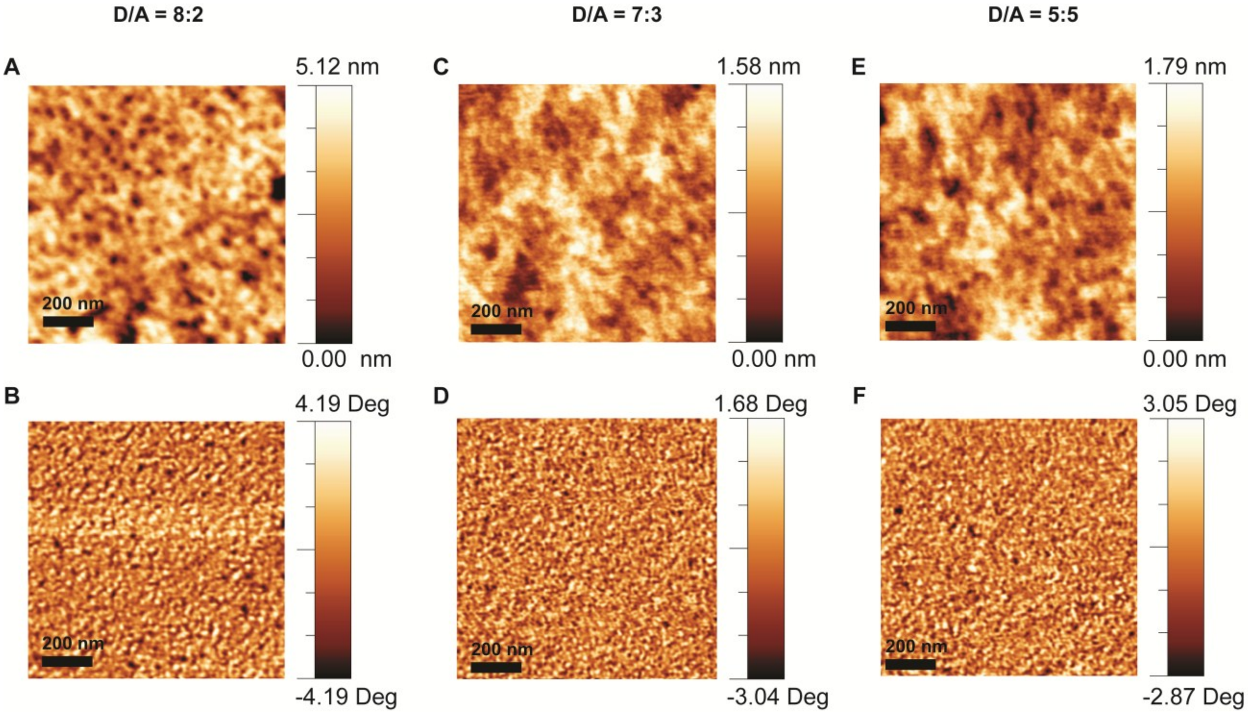

Fig. S5: AFM of the active layers of **DPPHP** devices processed from chlorobenzene solutions at different donor/acceptor ratios

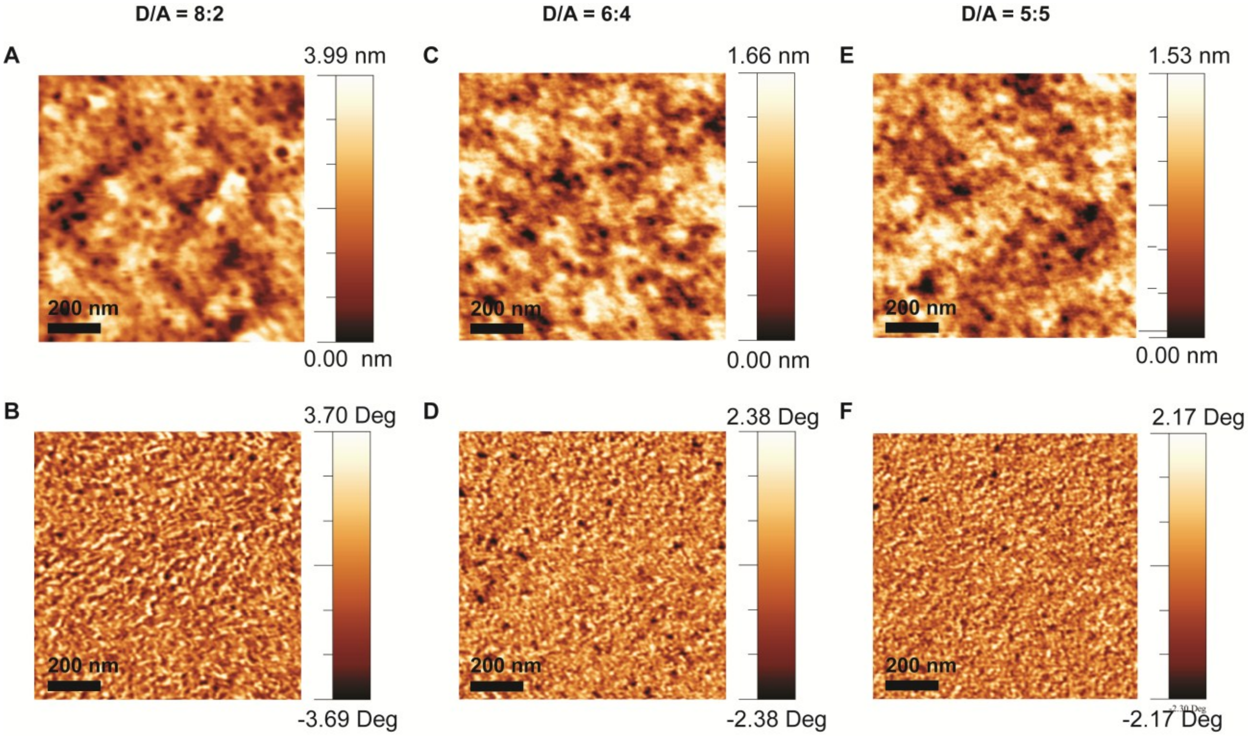

Fig. S6: AFM of the active layers of **DPPHP** devices processed from toluene solutions at different donor/acceptor ratios. (Height images in the top row, phase images in the bottom row).

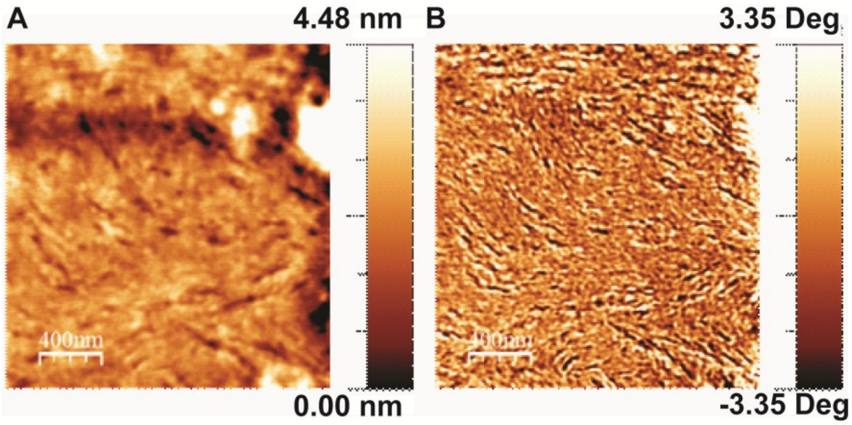

Fig. S7: AFM height (**A**) and phase (**B**) images of a thin film spin cast from an assembled solution of **DPPHP** which was stirred for 12 hours. The fibers are shorter and less bundled. The scale bar is of 400 nm in both images.

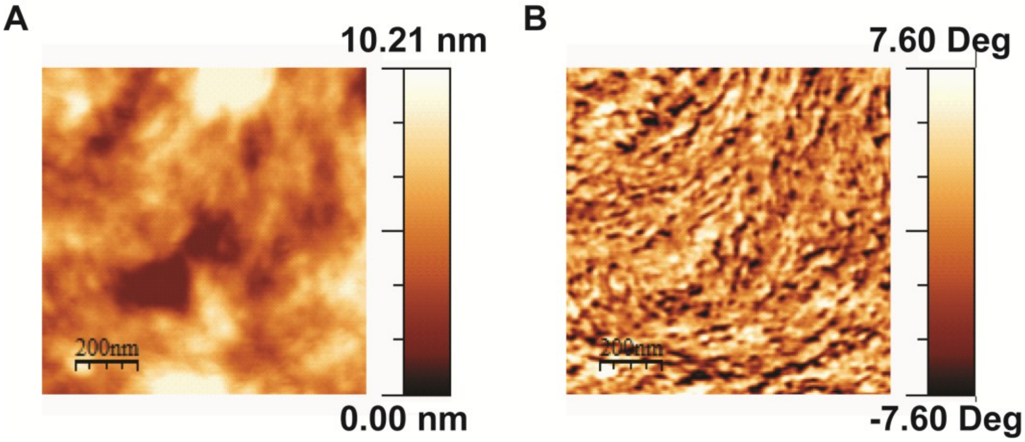

Fig. S8: AFM height (**A**) and phase (**B**) images of a thin film spin cast from **LDM** in toluene. The solution was prepared by the gradual cooling method. The scale bar is 200 nm in both images.

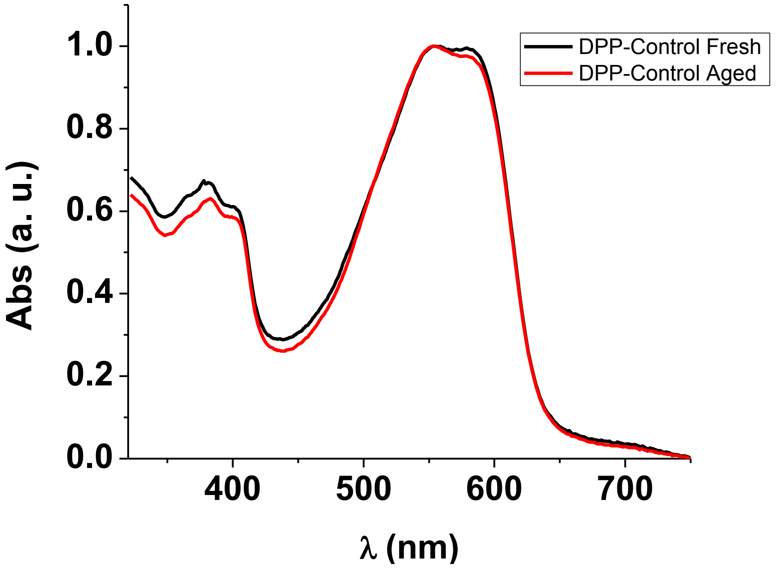

Fig. S9: UV-vis spectra of fresh and aged **LDM** solutions in toluene. There are no signs of aggregation after aging.

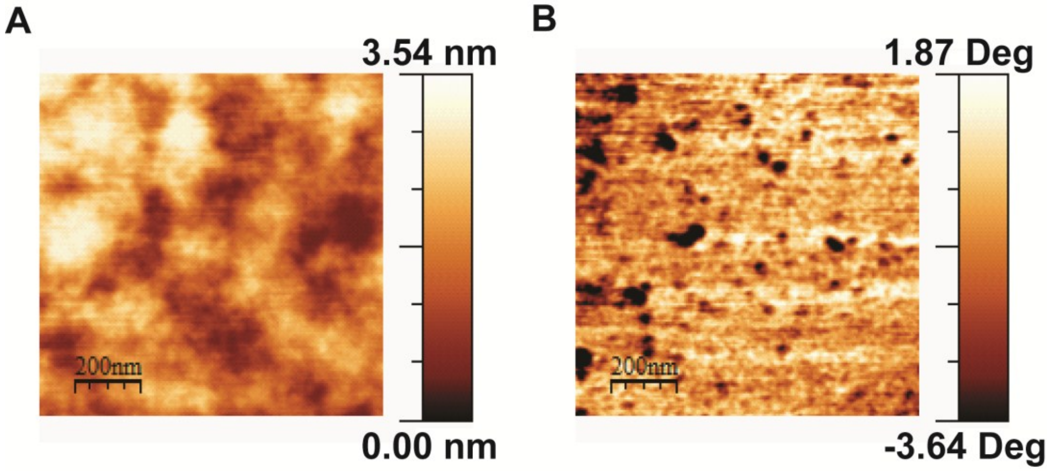

Fig. S10: AFM height (**A**) and phase (**B**) images of the active layer of a **LDM** device. The **LDM** solution was prepared in toluene by the gradual cooling method and mildly mixed with **PC$_{71}$BM**. The scale bar is 200 nm in both images.

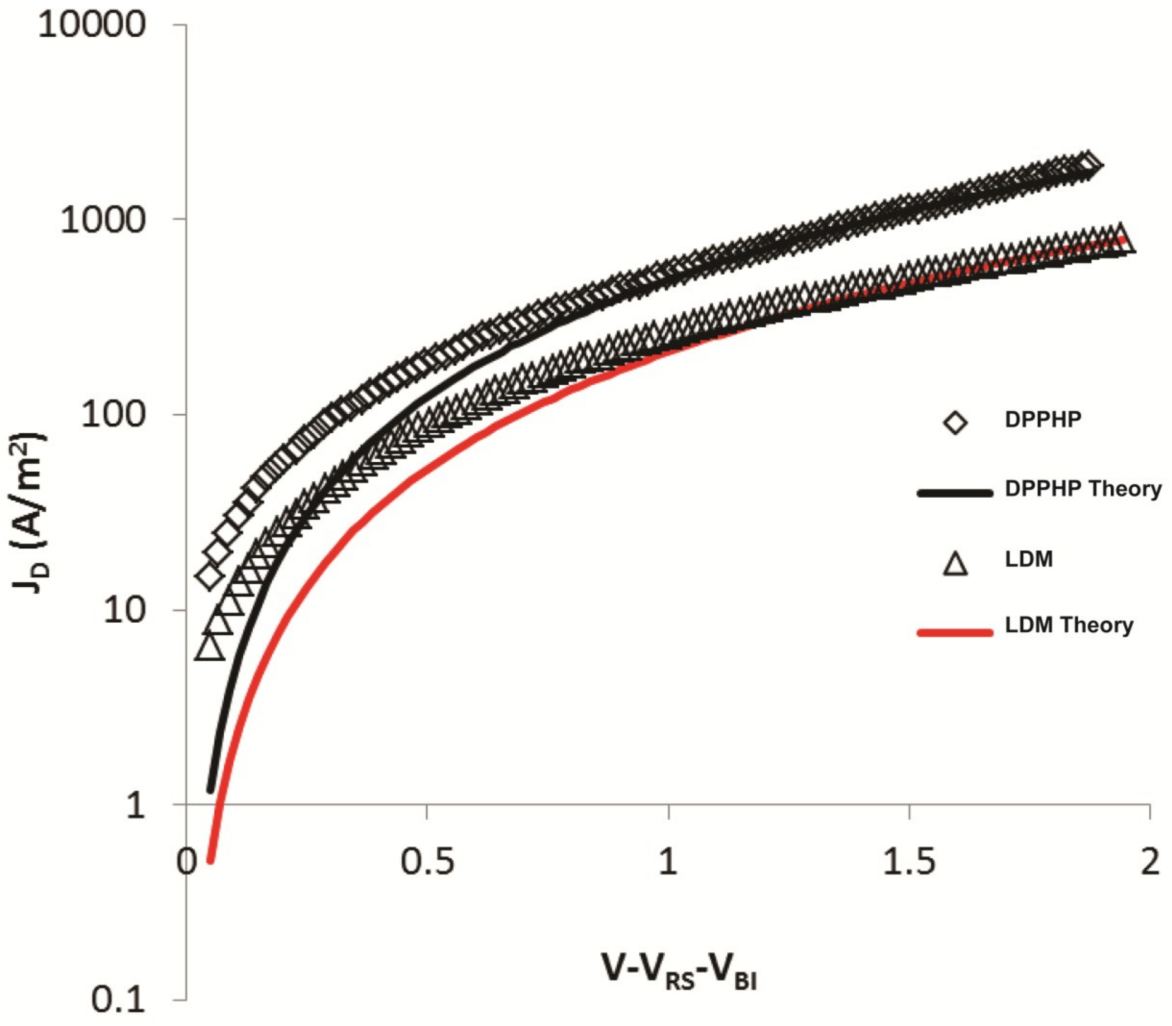

Fig. S11: Experimental dark-current densities (J_D) for **DPPHP:PC$_{71}$BM** and **LDM:PC$_{71}$BM** film blend devices at room temperature superimposed with curves calculated by the Child's law.