

## Supporting Information

### **Modulating Molecular Aggregation by Facile Heteroatom Substitution of Diketopyrrolopyrrole based Small Molecules for Efficient Organic Solar Cells**

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### **Instruments and measurements**

*UV-Vis measurement:* UV-Vis absorption spectra were measured with a Perkin Elmer Lambda 900 UV-Vis-NIR absorption spectrometer.

*Electrochemical measurements:* The electrochemical measurements were performed with a PGSTAT30 potentiostat (Autolab, Netherland) employing a conventional three-electrode electrochemical cell. A platinum disk electrode (BAS, USA) of 1 mm diameter was used as the working electrode, a platinum wire as the auxiliary electrode, and a silver wire modified with silver chloride as the pseudoreference electrode. Square wave voltammetry (SWV, amplitude 25 mV, step potential 5 mV, 20 Hz) was utilized for the measurements in 0.1M TBAClO<sub>4</sub> solution in acetonitrile as supporting non-aqueous electrolyte. The electrolyte solution was degassed for at least 20 min with high-purity nitrogen and kept under a blanket of argon during all electrochemical experiments. Prior to use the platinum working electrode was pretreated by cyclic voltammetry in 0.1M KCl (from -1.3 V to 1.9 V, scan rate 50 mV/s). Then the working electrode has been modified via drop casting of 5 mkl of chloroform solution of appropriate compound followed by quick drying. The working electrode cleaning and modification have been repeated each time before the measurement. In order to define the

applied potential, SWV curve has been recorded after the addition of ferrocene into the electrochemical cell at the end of measurements.

*GIWAXS measurement:* Films used for XRD were spun on silicon with native oxide. X-ray scattering was performed at the Stanford Synchrotron Radiation Lightsource (SSRL) on beam line 11-3 (2D scattering with an area detector, MAR345 image plate, at grazing incidence) with an incident energy of 12.7 keV. The incidence angle (0.12 degrees) was chosen to be slightly larger than the critical angle of the polymer film, ensuring that we sampled the full film depth.

*OFET Device Fabrication and Characterization:* Glass substrates were cleaned sequentially in water, acetone and isopropanol for 10 min each, following by drying using a stream of nitrogen. Source-drain electrodes patterns were fabricated using a conventional evaporation procedure through metal shadow mask (channel length 30  $\mu\text{m}$ , channel width 500  $\mu\text{m}$ ). 5-nm-thick Ti was used as adhesion layer of the Au electrodes on glass. M1 and M2 were separately dissolved in Chloroform at a concentration of 5 mg/mL. The solutions were spin coated onto the glass substrates at 1000 rpm for 60 s. Then the films were thermally annealed at 90  $^{\circ}\text{C}$  under nitrogen atmosphere for 30 min and cooled down to room temperature naturally. The dielectric polymer PTrFE (Solvay SA) was dissolved in acetonitrile to form a 60 mg/mL solution, then spin coated on top of the M1 and M2 films at 2000 rpm for 60 s, yielding a dielectric thickness of 500-600 nm. After the dielectric layers were deposited, the devices were baked at 80  $^{\circ}\text{C}$  under nitrogen atmosphere for 30 min and cooled down to room temperature. Finally, the devices were completed by evaporating a 70-nm-thick Al gate electrode through a metal shadow mask on top of the dielectric layers. All the OFET electrical characteristics were measured using a Keithley 4200-SCS in air.

*PV device fabrication and characterization:* The BHJ photovoltaic devices were fabricated with a device geometry of Glass/ITO/PEDOT:PSS(40 nm)/Active Layer/LiF(0.6 nm)/Al(90 nm). The ITO coated glass substrates were cleaned by using acetone and detergent. The substrates were then treated by TL-1, which is the mixture of water, ammonia (25%), and hydrogen peroxide (28%) (5:1:1 by volume). PEDOT:PSS 4083 (Heraeus Precious Metals GmbH & Co. KG) was spin-coated atop the cleaned substrates and heated for 20 minutes at 120  $^{\circ}\text{C}$  to remove the remaining water. Then, the substrates coated with PEDOT:PSS 4083 were moved into glove box filled with  $\text{N}_2$ . The active layers were spin-coated from chloroform solutions (M1:PC<sub>61</sub>BM=1:1 (w/w), 15 mg/mL;

M2:PC<sub>61</sub>BM=1:1 (w/w), 20 mg/mL) onto the substrates. Then, the substrates were transferred into a vacuum chamber mounted in the glove box, where 0.6 nm LiF and 90 nm Al were thermally evaporated through a shadow mask under a pressure less than 5×10<sup>-6</sup> mbar. For the hole-only devices, LiF/Al top electrode in the normal structure was replaced by MoO<sub>x</sub> (8 nm)/Al (100 nm). The active area for the PV device defined by the overlap area between ITO anode and metal cathode is about 0.045 cm<sup>2</sup>, which is calibrated by optical microscopy. The *J-V* curves were characterized by using a Keithley 2400 Source Meter under AM1.5 illumination provided by a solar simulator (Model SS-50A, Photo Emission Tech., Inc.) with an intensity of 1000 W m<sup>-2</sup>. EQE spectra were measured using a Newport Merlin lock-in. The chopped monochromatic light was illuminated on the solar cells through the ITO side. The thickness of the active layers was obtained by a Dektak surface profiler.

*CT state absorption by FTPS*: FTPS-EQE were measured by using a Vertex 70 from Bruker optics. E<sub>CT</sub> is obtained by fitting the low energy part of the EQE spectrum using Equation<sup>[1]</sup>:

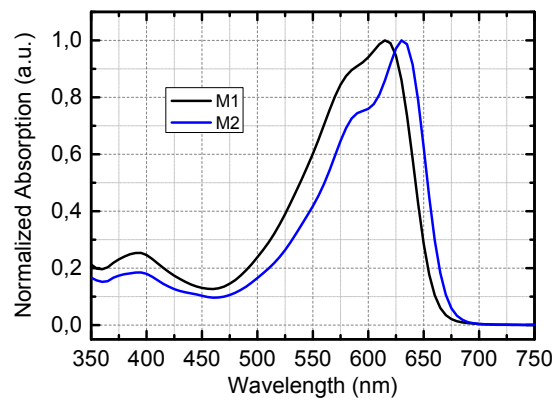
$$EQE_{CT}(E) = \frac{\eta N_{CTC} 2df_{\sigma}}{E \sqrt{4\pi kT}} \exp\left(\frac{-(E_{CT} + \lambda - E)^2}{4\lambda kT}\right)$$

*SCLC Measurements*: The hole only devices were fabricated with the configuration of ITO/PEDOT:PSS/active layer/MoO<sub>3</sub>/Al. The active layer was spin-coated on the PEDOT:PSS layer to same method with photovoltaic device fabrications. Charge carrier mobilities  $\mu$  can thus be deduced from the Equation <sup>[2]</sup>:

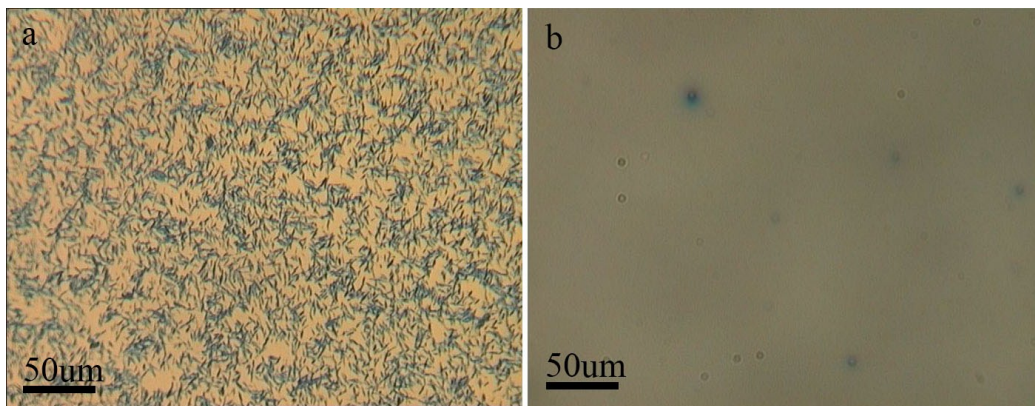
$$J = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{(V - V_{bi})^2}{d^3}$$

where  $J$  is the current density,  $\epsilon$  and  $\epsilon_0$  are the relative and vacuum permittivity,  $\mu$  is the hole mobility and  $d$  is the thickness of the active layer. In this equation, we assume  $\epsilon$  equals 3.

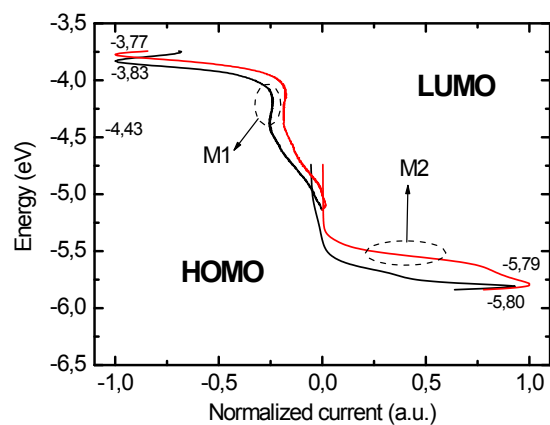
*PL measurements*: PL spectra were recorded by using an Andor spectrometer (Shamrock sr-303i-B, coupled to a Newton EMCCD detector). The pumping light source used to measure PL is a blue laser (CW He-Ne 405 nm) with an intensity of 2 mW cm<sup>-2</sup>.



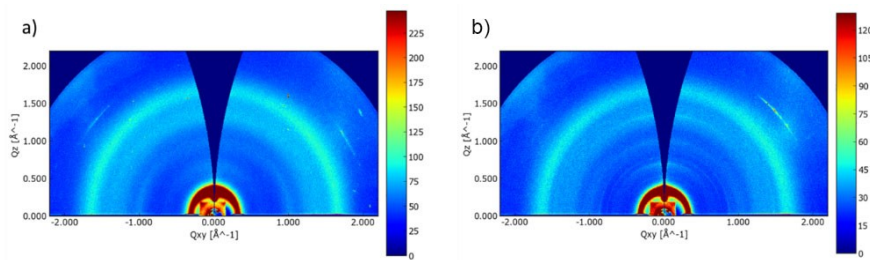
**Figure S1.** UV-vis spectra of M1 and M2 in chloroform



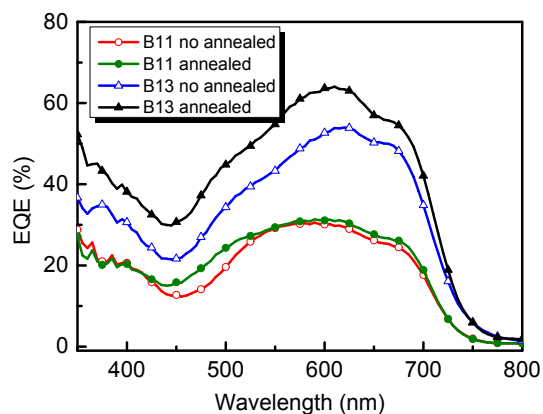
**Figure S2.** Optical microscope images of M1(a) and M2 (b) thin films spin coated from chloroform solution.



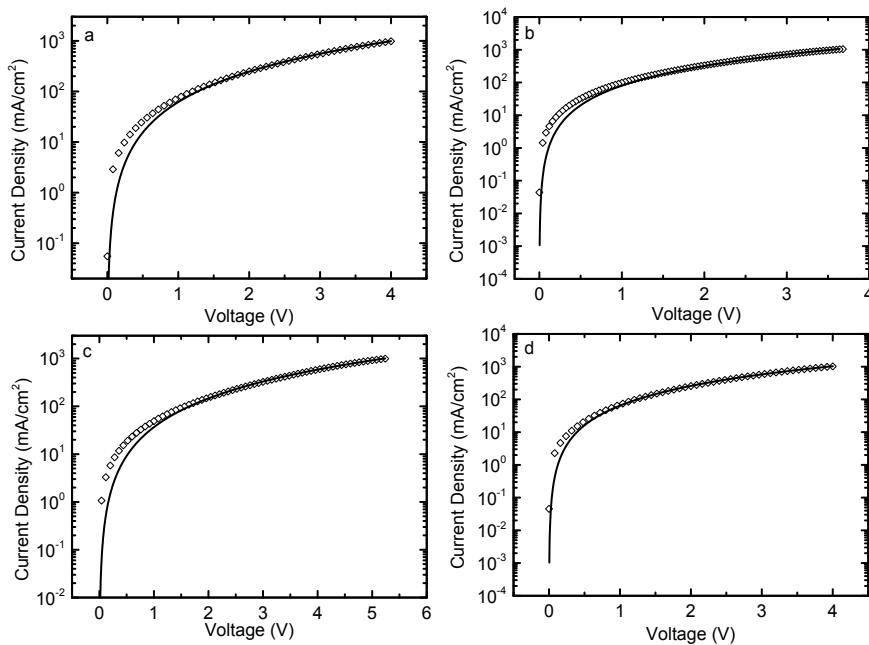
**Figure S3.** Square wave voltammetry of materials M1 (dashed), M2 (dash dot) and PC<sub>61</sub>BM (solid)

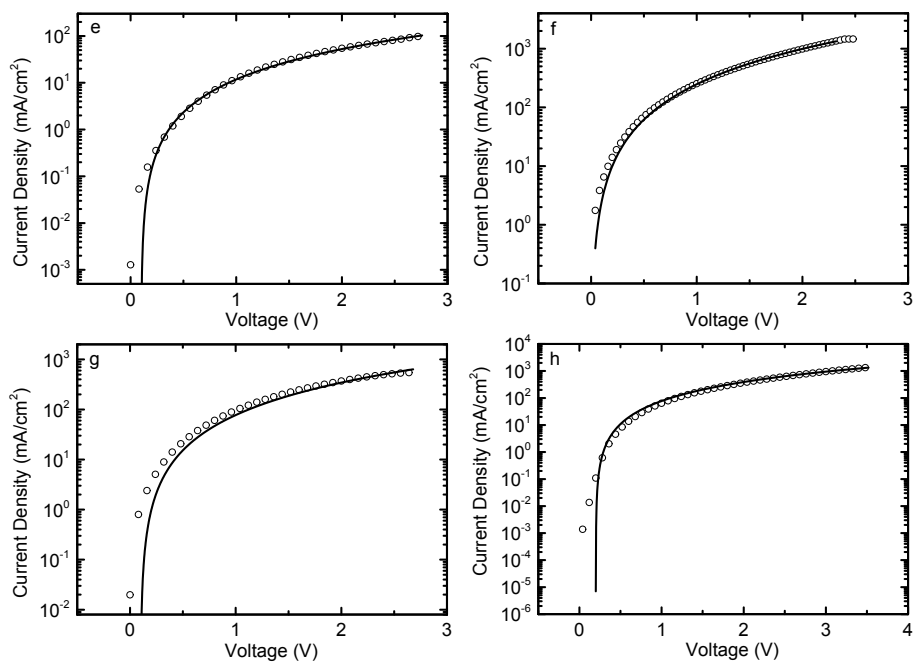


**Figure S4.** GIWAXS patterns of M1 (a) and M2 (b) films spin-coated from CF solutions



**Figure S5.** EQE curves of the corresponding solar cells.





**Figure S6.** Experimental (symbols) and fitting curves (solid lines)  $J$ - $V$  characteristic of the blend films in hole only device configuration viz. ITO/ (PEDOT:PSS) /active layer/MoO<sub>3</sub>/Al, M1:PC<sub>61</sub>BM as cast film (a) and annealed film (b); M2:PC<sub>61</sub>BM as cast film (c) and annealed film (d); in electron only device configuration viz. ITO/PEIE/active layer/LiF/Al, M1:PC<sub>61</sub>BM as cast film (e) and annealed film (f); M2:PC<sub>61</sub>BM as cast film (g) and annealed film (h).

[1] Koen Vandewal, Kristofer Tvingstedt, Abay Gadisa, Olle Inganäs, Jean V. Manca, *Phy. Rev. B* **2010**, 81, 125204.

[2] P. W. M. Blom, M. J. M. de Jong, J. J. M. Vleggaar, *Appl. Phys. Lett.* **1996**, 68 (23), 3308-3310.