Electronic Supplementary Information for

Anomalous high photovoltages observed in shish kebab-like organic p-n junction nanostructures

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1. Synthesis of C5-PTCDI. C5-PTCDI was synthesized following the same method previously reported by our group.[1] Briefly, 0.2 g (0.54 mmol) perylene-3,4,9,10-tetracarboxylic dianhydride, 0.5 mL cyclopentylamine, and 5 g imidazole were mixed together and then heated under argon at 120 °C for 4 h in a flask. The reaction mixture was naturally cooled to room temperature and dispersed in 30 mL ethanol followed by addition of 20 mL concentrated HCl solution and 30 mL distilled water. The mixture was stirred overnight, and then the resulting red solid was collected by vacuum filtration through a 0.45 µm membrane filter (Osmonics). Subsequently, it was washed thoroughly with distilled water until the pH of washings became neutral. The collected solid was dried in vacuum at 60 °C, followed by further purification through silica gel column chromatography (eluent: chloroform).

2. Preparation of C5-PTCDI elongated single crystals. Self-assembly of C5-PTCDI into elongated crystals were accomplished by slowly evaporating the C5-PTCDI/chloroform solution (0.3 mg/mL) under ambient condition.

3. Preparation of C5-PTCDI/P3HT shish kebab-like structure. The shish kebab-like structures were made as followings: **(1)** 4 mg of highly regioregular P3HT (with M_n of ~20kDa, PDI of 2.0, and regioregularity better than 95% , Rieke Metals Inc.) was dissolved in 1 mL anhydrous xylene at 60℃ to form homogenous solution. **(2)** quickly cooled down the above P3HT/xylene solution to room temperature, and then 1.0 mg of the C5-PTCDI elongated single crystals were added into the P3HT/xylene solution, shook well and kept the suspension in quiet condition for 2 days. Most of the C5-PTCDI single crystals were still preserved in the solution as the solubility of C5-PTCDI in xylene is very low. Because P3HT will crystallize in xylene when cooled down to room temperature, some P3HT will epitaxially grow on the surface of C5-PTCDI single crystals due to the matched crystalline lattice between P3HT and PTCDI. After two days, the shish kebabs structures are formed.

4. Preparation of the solar cells based on individual shish kebab-like p-n junction. (1) Shake well the above obtained suspension of C5-PTCDI/P3HT shish kebab in xylene, and then 5 μl of the suspension was diluted into 0.2 mL xylene. (2) The dilute suspension was spun cast on clean glass slide at a spin coating speed of 2000 rpm to ensure sparse distribution of the shish-kebab structures. (3) Shadow mask was placed on a selected shish kebab structure, followed by atop deposition of Au and Al electrodes in high vacuum.

5. preparation of the bulk-heterojunction based solar cells. These solar cells were fabricated under ambient conditions following the similar device fabrication procedures reported eleswhere.[2] First, a 50 nm PEDOT:PSS layer was spun cast onto a pre-cleaned glass substrate covered with 120 nm pre-patterned indium tin oxide (ITO) conductive layer (with sheet resistance of 10 Ω/□). Second, the photoactive layer was deposited by spin coating the prepared suspension or solution to a thickness of ca. 110-150 nm. Finally, the devices were completed with cathode deposition by thermal evaporation of 100 nm Al.

6. Characterization. AFM measurements were conducted on a Veeco MultiModeV SPM instrument in intermittent contact (tapping) mode. Images were acquired with 512×512 points and scanning rate of ~ 0.5 Hz per line. Transmission electron microscopy (TEM) images were acquired on a JEOL 2010 TEM. Scanning Electron microscopy (SEM) characterization was conducted on a FEI Nano Nova 630 SEM. Solar cells were tested using an Agilent 4156C Precision Semiconductor Parameter Analyzer in ultrahigh purity Argon.

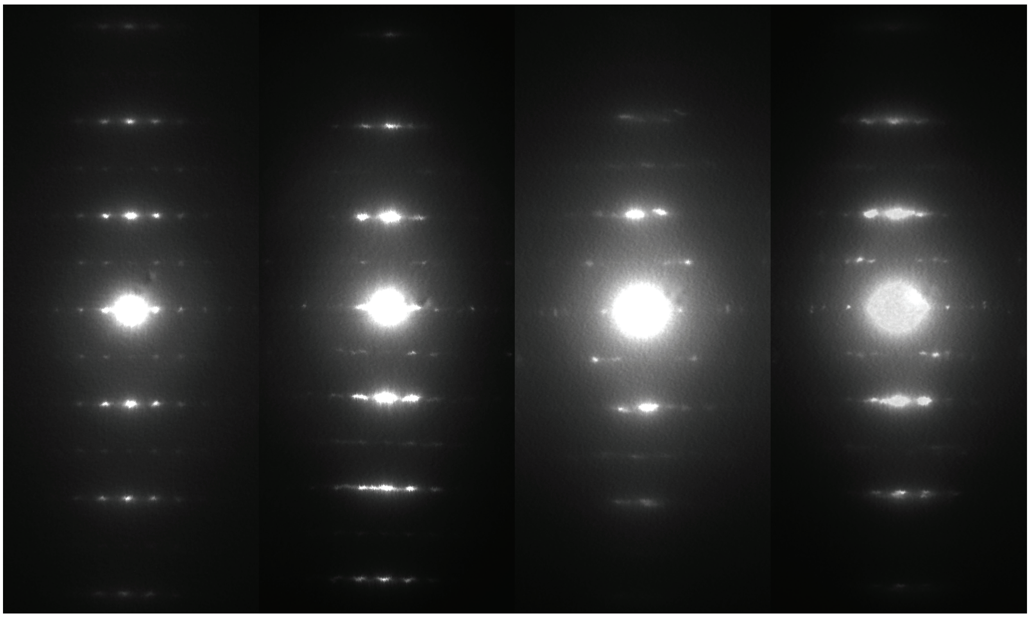

Figure S1. The same SAED patterns were obtained on different spots of a C5-PTCDI belt, indicating the single-crystalline nature.

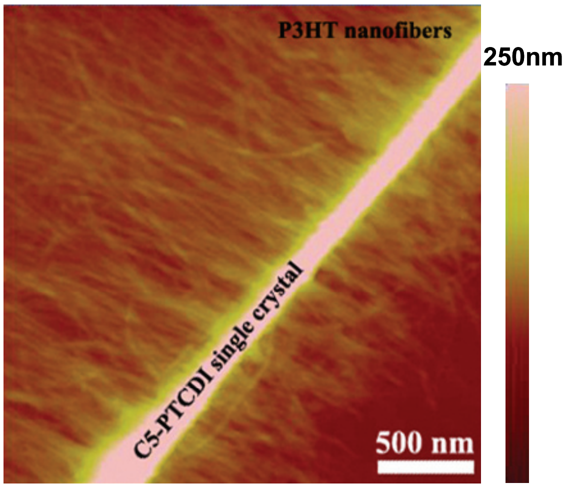

Figure S2. AFM topography image showing the growth details of C5-PTCDI/P3HT shish kebab-like structure.

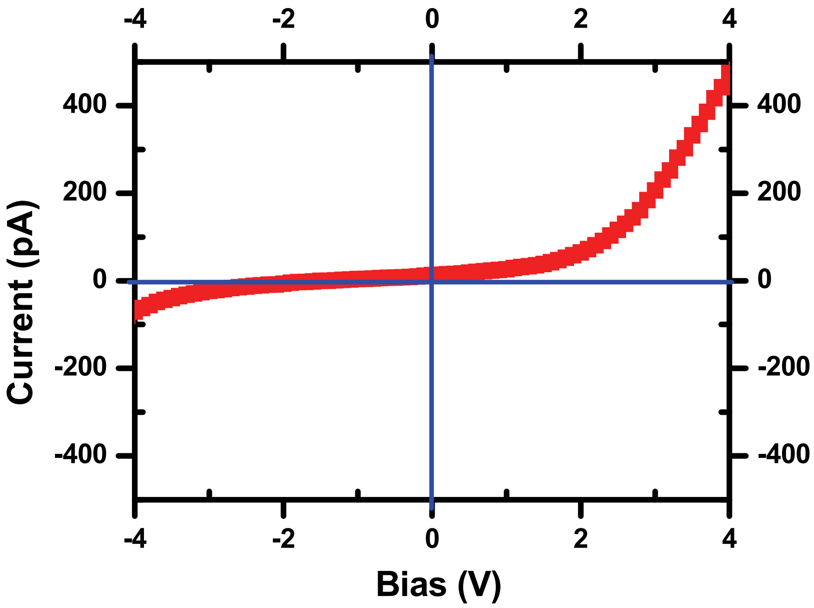

Figure S3. I-V plot showing the rectification property of a device based on C5-PTCDI/P3HT shish kebab-like p-n junction. The measurement was conducted in dark. The gap distance between Au and Al electrode in this device is 40μm.

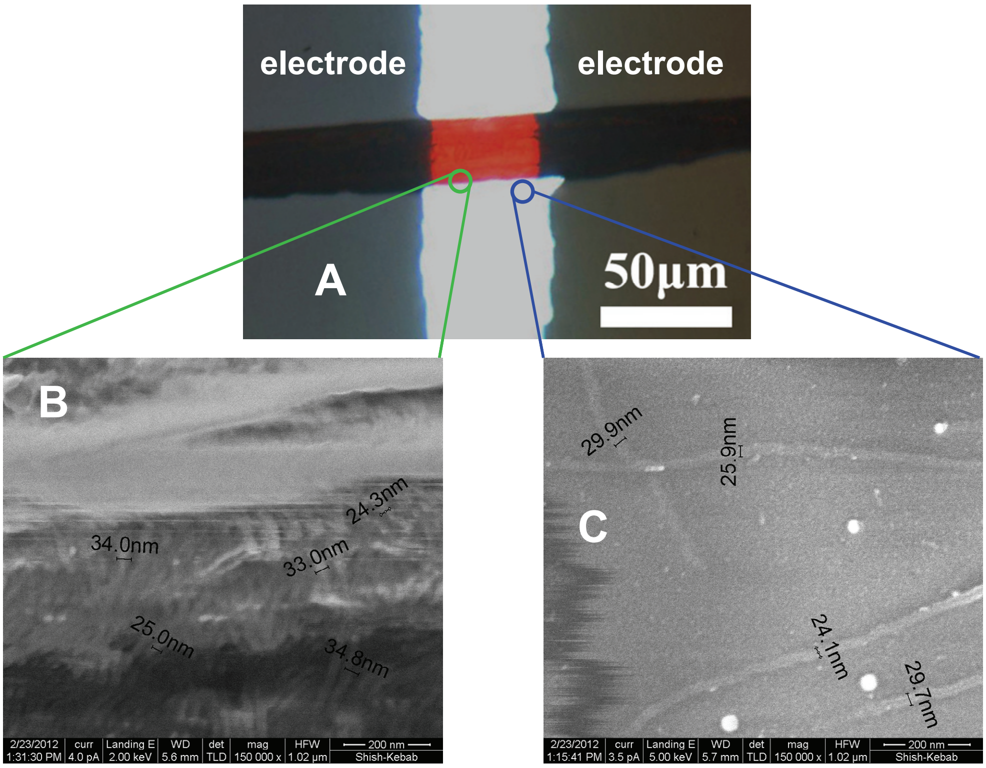

Figure S4. optical (A) and SEM (B) images verifying the shish kebab morphology of the photoactive part in a horizontal PV device. (C) SEM image showing that there are sporadic P3HT fibers on the glass substrate, indicating that there is neglectable continuous hole transport paths except for those on shish kebab-like structure.

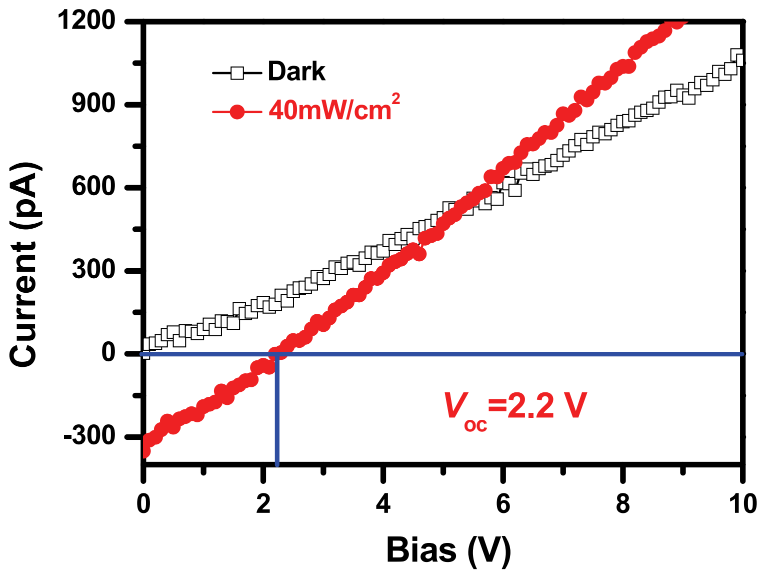

Figure S5. I-V curves of a horizontal PV device based on a shish kebab-like p-n junction tested under dark and simulated AM1.5G illumination at 40mW/cm^2. Electrode gap distance of the device is 80μm.

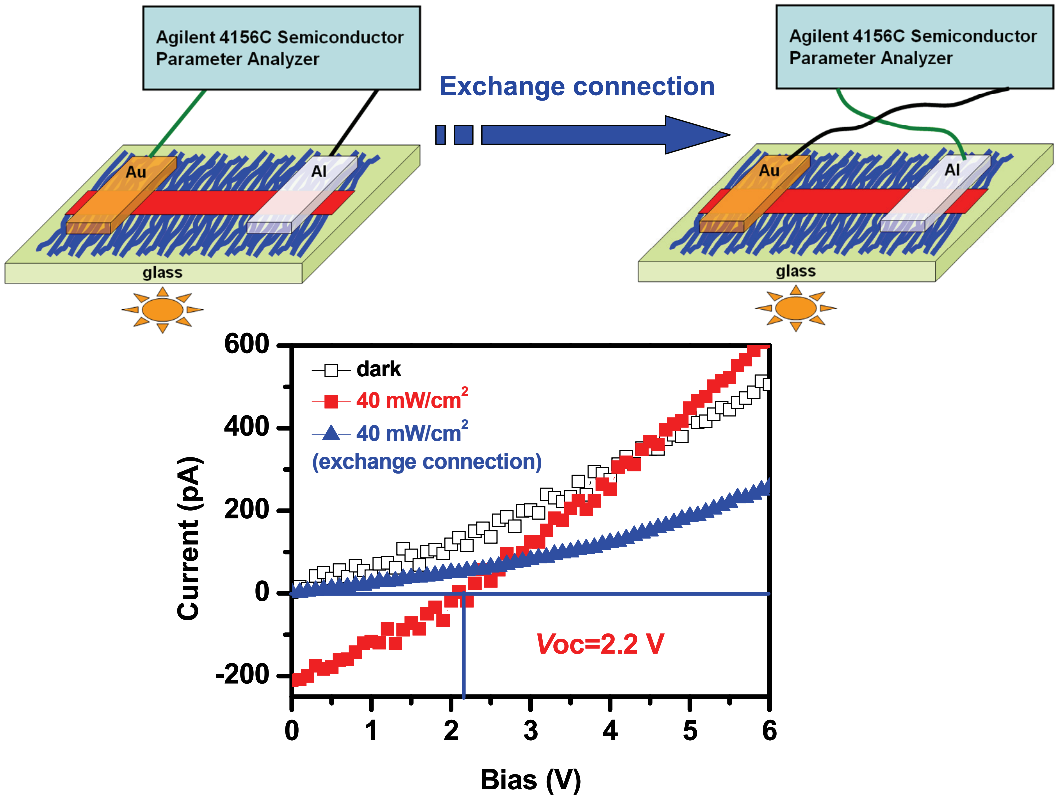

Figure S6. *Top:* sketches showing the connection exchange when testing a horizontal PV device based on a shish kebab-like p-n junction. *Bottom:* I-V curves of the corresponding solar cell device tested under dark, simulated AM1.5G light illumination at 40mW/cm^2 with and without exchanging connection. Electrode gap distance of the device is 40 μm. As shown in the plot, V_{oc} of 2.2V can be observed under forward bias. However, no photovoltage can be observed in the reverse bias (achieved by exchanging the connection shown above), a property in the photovoltaic diode, indicating that the V_{oc} obtained here is indeed the photovoltage of a solar cell device.

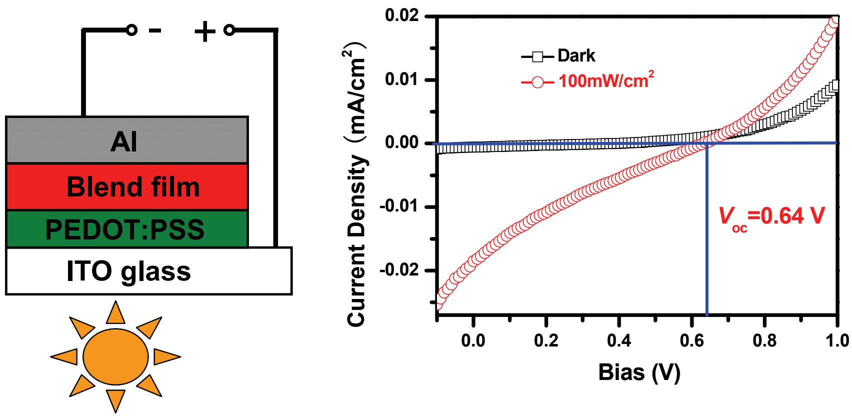

Figure S7. Bulk-heterojunction solar cell based on the blend film of P3HT and C5-PTCDI. *Left:* device structure; *Right:* the corresponding J-V curves under dark and simulated AM1.5G illumination at 100mW/cm^2.

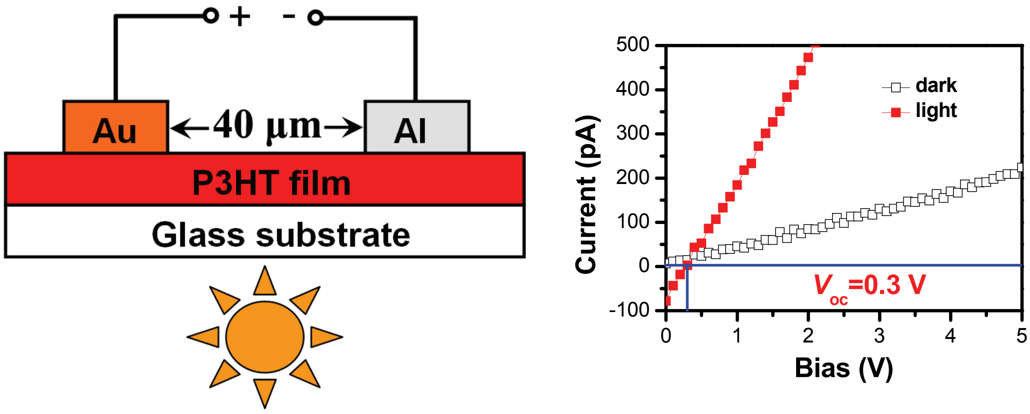

Figure S8. The device structure of a P3HT film only photovoltaic device (with a P3HT film thickness of 100nm) and the corresponding I-V curves under dark and simulated AM1.5G illumination at 40mW/cm^2.

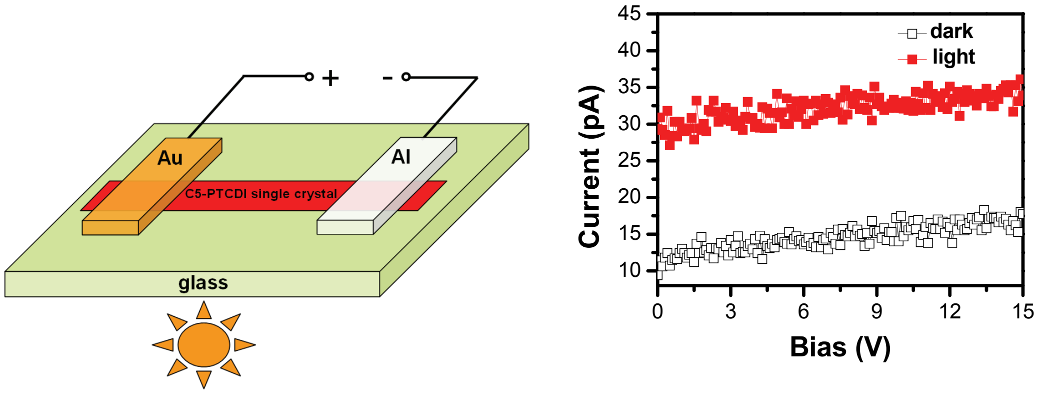

Figure S9. The device structure of a C5-PTCDI single crystal only photovoltaic device (with a electrode gap distance of ca. 40 μm) and the corresponding I-V curves under dark and simulated AM1.5G light illumination at 40mW/cm^2. As we can see in the I-V curves, there is no photovoltaic effect in the C5-PTCDI single crystal only device.

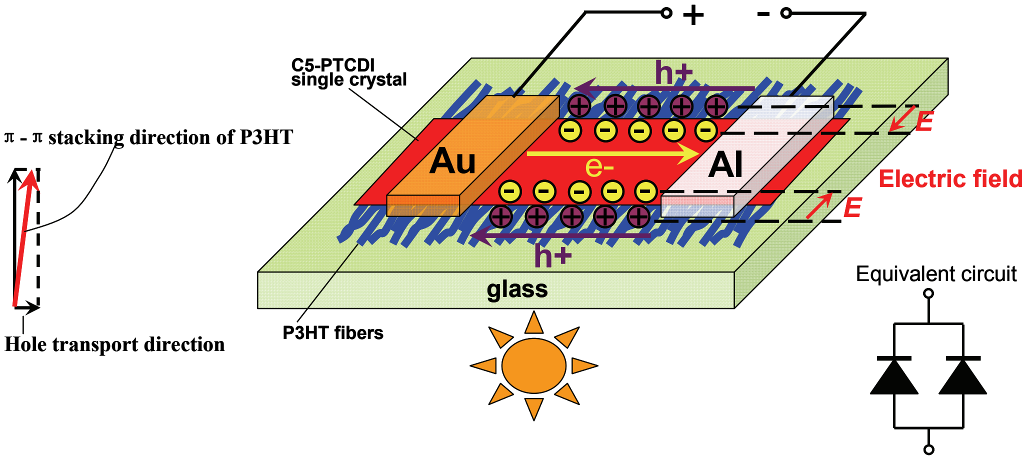

Figure S10. Sketch showing possible explanation of high V_{oc} observed in horizontal photovoltaic devices based on a shish kebab-like p-n junction of C5-PTCDI/P3HT. The presence of large amount of charge carriers on both sides of C5-PTCDI single crystal may form a balanced electric field and set up a net voltage across the interface between P3HT nanofibers and C5-PTCDI single crystal, leading to formation of a new photovoltage which is not determined by the energy level offset between the LUMO of C5-PTCDI and the HOMO of P3HT. Consequently, it is anticipated that a photovoltage higher than the theoretical upper limit can be observed when certain amount of charges accumulated at the interface between P3HT and C5-PTCDI.

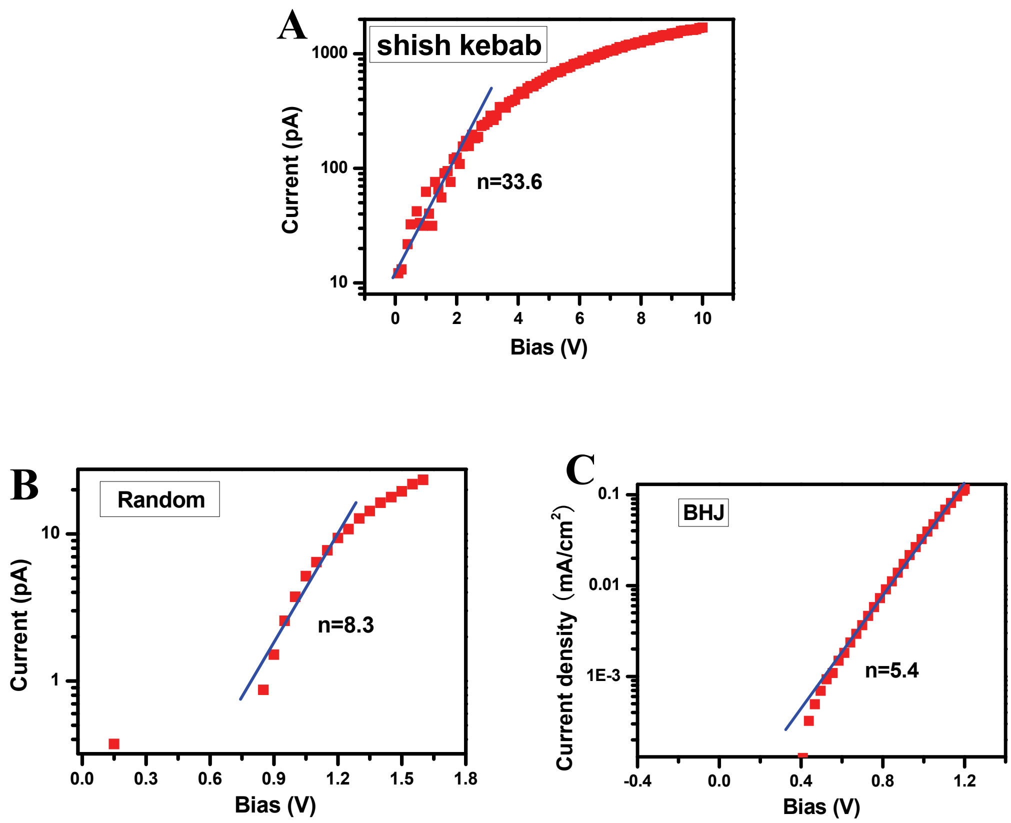

Figure S11. A logarithm plot of dark current vs bias of the devices shown in Fig. 3, (A) shish kebab-like p-n junction, indicated as shish kebab; (B) PV device based on a C5-PTCDI single crystal covered by random P3HT fibers, indicated as random; (C) BHJ solar cell employing the traditional sandwich structure with C5-PTCDI/P3HT shish kebab-like structures as the photoactive layer, indicated as BHJ. The diode ideality factors *n* can be calculated from the linear fit part indicated by the blue solid line in each plot. A remarkable ideality factor n of 33.6 is observed for the shish kebab device. As for the origin of rather large ideality factor, it is still not very clear in literature.[3-10] Ideality factors of 8.3 and 5.4 are extracted for random and BHJ devices, respectively. The relatively large ideality factors observed in random and BHJ devices are usually the sum of the ideality factor of individual rectifying junctions[11-14] (i.e. the Al/C5-PTCDI, C5-PTCDI/P3HT and P3HT/Au junctions in our case).

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