

## Supporting Information

### Organic photovoltaic featuring graphene nanoribbons

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### Experimental Section

*Synthesis of graphene nanoribbons (GNRs) and printing:* The process for creating graphene nanoribbons is similar to that developed by the Tour group.<sup>15,16</sup> Using a 1 L Erlenmeyer flask with matching stopper, 35 mg of MWNTs was dispersed in 35 mL of concentrated H<sub>2</sub>SO<sub>4</sub> (99.999%, Sigma Aldrich) and stirred overnight. The MWNTs diameter ranger from 30 – 50 nm, and a length of 30 μm, carbon purity is > 95%, and –COOH functionalization is < 4%. Then 4 mL of H<sub>3</sub>PO<sub>4</sub> (≥ 99.999%, Sigma-Aldrich) was added to the mixture of carbon nanotubes and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>:H<sub>3</sub>PO<sub>4</sub> final volume ratio of 9:1) and stirred for 15 min. Immediately thereafter, 0.34 g (8.5 wt equiv) of KMnO<sub>4</sub> (≥ 99%, Sigma Aldrich) was added to this mixture, and the reaction was heated at 65 °C for 1 h. The reaction was stopped by placing the flask into an ice bath (~200 mL) containing 3 mL of H<sub>2</sub>O<sub>2</sub> (30 wt % in H<sub>2</sub>O, Sigma Aldrich). The mixture was filtered over a 0.5 μm pore size poly(tetrafluoroethylene) (PTFE) membrane filter (Supelco) and then successively washed and filtered twice with 200 mL of 30% HCl (36.5-38%, ≤ 1 ppm chlorine free, Sigma Aldrich) and 200 mL of deionized water (≥ 98% HPLC, Sigma Aldrich). The resulting graphene oxide nanoribbons were first redispersed in 40 mL of deionized water by stirring overnight. They were then placed into SnakeSkin dialysis tubing (10 K molecular weight cutoff (MWCO), Fisher), dialyzed for 14 days to remove impurities from the inorganic acids and oxidized by a salt oxidizing mixture. Several steps of continuous sonication and ultracentrifugation were eliminated during the purification of the nanoribbons to avoid cutting the nanoribbons which would reduce the aspect ratio of the nanoribbons. After dialysis process, the suspension of graphene oxidized nanoribbons in water was filtered through a 0.5 μm pore size PTFE membrane filter. The solid obtained on the membrane filter was vacuum-dried overnight at room temperature to obtain approximately 24 mg of product along with the yield of about ~70%.

To reduce graphene oxide nanoribbons chemically, a 8 mL suspension of graphene oxide nanoribbons was dispersed in deionized water and was centrifuged (3000 rpm) for 30 min to provide a nanotube concentration of 3 mg/mL, which was then poured into a 100 mL two-neck round-bottom flask that was equipped with a stir bar, a reflux condenser, and a septum inlet containing 72 mL of anhydrous N,N-dimethylformamide (99.8%, Sigma-Aldrich). Then 4 μL of hydrazine monohydrate (N<sub>2</sub>H<sub>4</sub>) (64-65%, Sigma-Aldrich) was added to the mixture and heated to 85 °C for overnight reflux. The reaction was then cooled to room temperature and used directly to prepare the electrodes by inkjet printing. The inkjet ink was produced using two steps of filtration through the PTFE membrane (5 μm). Thermal reduction was performed in a 5 %

hydrogen/argon environment at 300 °C for 2 h, and then the graphene nanoribbons were deposited onto the substrate.

*Ink preparation:* An aqueous solution combining 1 mg/mL of graphene nanoribbons and 3 mg/mL of sodium n-dodecyl sulfate (SDS), an anionic surfactant was prepared and sonicated for 1 h. Then, the graphene nanoribbons ink was centrifuged at 10,000 rpm for 10 min and the supernatant was later removed. Finally, the supernatant was injected into a customized Autodrop pipette and printed using Autodrop Professional Positioning System AD-P-8000.

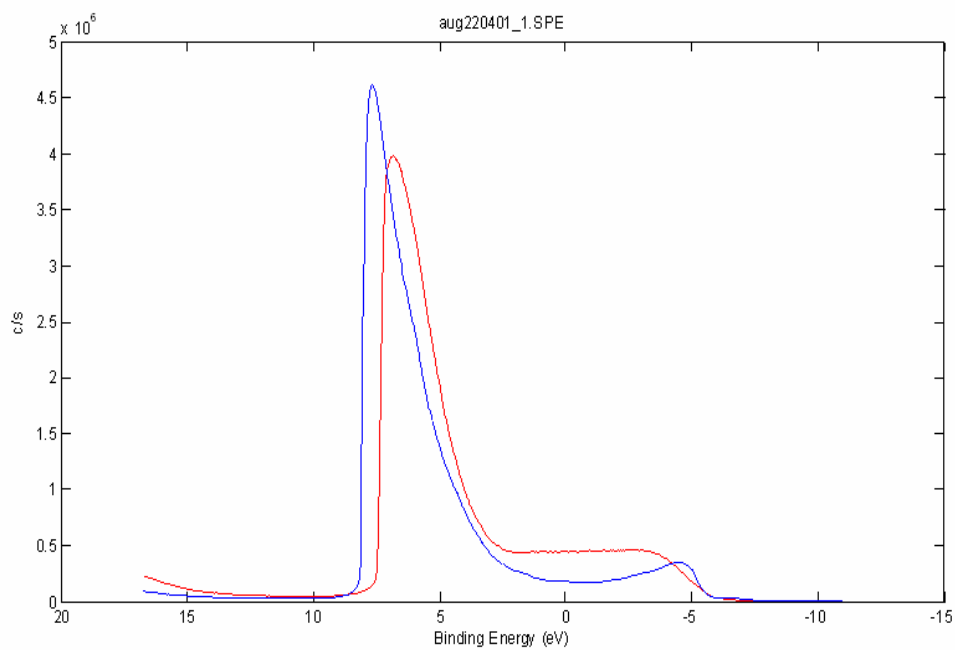
*Fabrication of solar cells:* The glass was prepared using a cleaning process including detergent, acetone, and isopropyl alcohol with ultrasonication. Then, the glass was exposed to UV-ozone (20 min) to reform the surface. Inkjet printing technology was executed using an Autodrop printer (Microdrop, Norderstedt, Germany) to print the graphene nanoribbons on the glass substrate with a thickness of around 40 nm (dried at 50 °C for 30 min). Then the PTB7:PC<sub>71</sub>BM BHJ active blend layer, with a nominal thickness of ~ 80 nm was prepared by spin-coating a mixed solvent of chlorobenzene/1,8-diiodooctane (97:3% by volume) solution (concentration, 25 mg mL<sup>-1</sup>) at 1000 rpm for 2 minutes. A 10 nm of C<sub>60</sub>-bis layer and a 100 nm of Ag layer were subsequently evaporated through a shadow mask to define the active area of the devices and form a top anode. The devices were encapsulated by a cleaned cover glass and a UV-curable epoxy in the N<sub>2</sub>-filled glove box.

*Measurement and characterization:* After calibration of the light source using silicon reference cells with an AM 1.5 Global solar simulator, the encapsulated BHJ solar cells were measured during the exposure of the devices to an intensity of 100 mW/cm<sup>2</sup> using a Keithley 236 source unit. Then, the J–V curves and PCE parameters (V<sub>OC</sub>, J<sub>SC</sub>, and FF) were obtained. To determine the exact cell areas, we used the aperture of 0.04 cm<sup>2</sup> on top of the deposited Al cathode while taking measurements. The morphology and surface roughness of BHJs with and without interlayers were determined by atomic-force microscopy (AFM; Veeco, USA; D3100) to confirm the contact of interlayers. The IPCEs were investigated by a QE measurement system (PV measurements, Inc.) after the calibration of monochromatic power density to check and match with the J–V characteristics.

For the UPS analysis, the PTB7:PC<sub>71</sub>BM BHJ was spin-casted onto the ITO-glass substrate. The films were dried at 80 °C for 10 minutes. The UPS analysis chamber was equipped with a hemispherical electron-energy analyzer (Kratos Ultra Spectrometer), and was maintained at 1.33 x 10<sup>-7</sup> Pa. UPS measurements were carried out using the He I (hν=21.2 eV) source. The electron-energy analyzer was operated at constant pass energy of 10 eV (for UPS). During UPS measurements, a sample bias of ~ 9 V was used in order to separate the sample and the secondary edge for the analyzer.

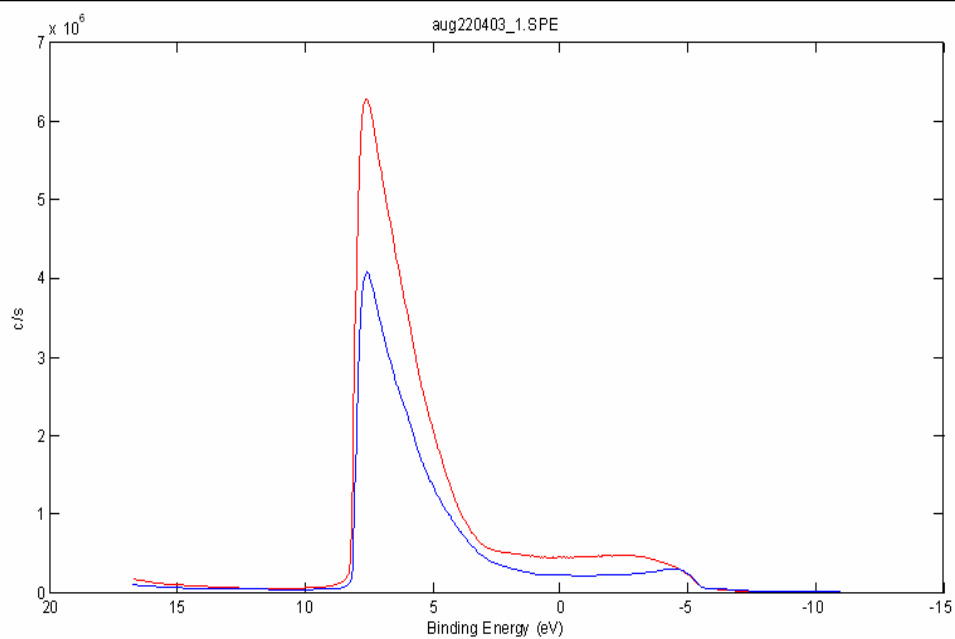
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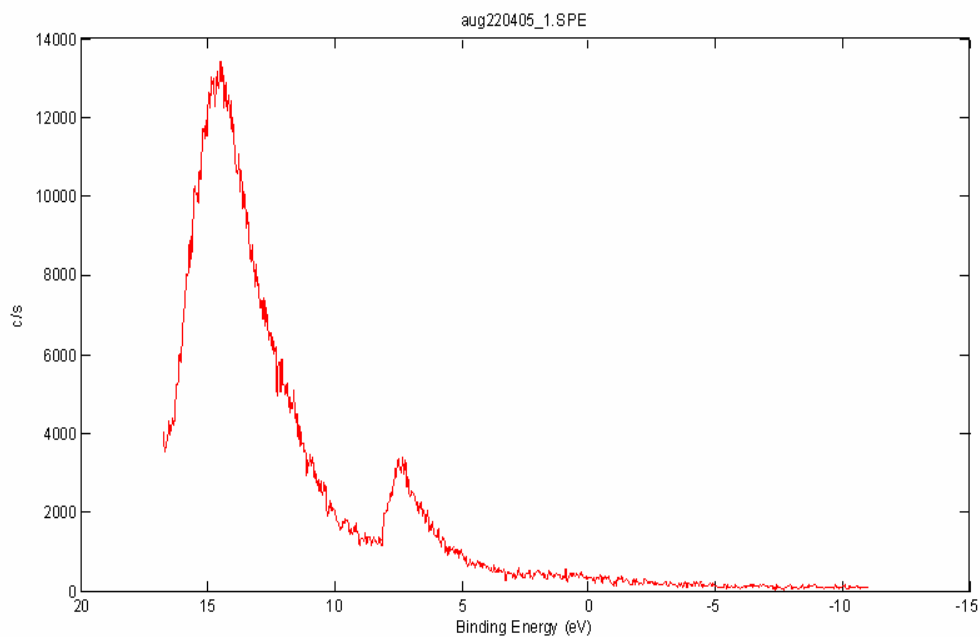


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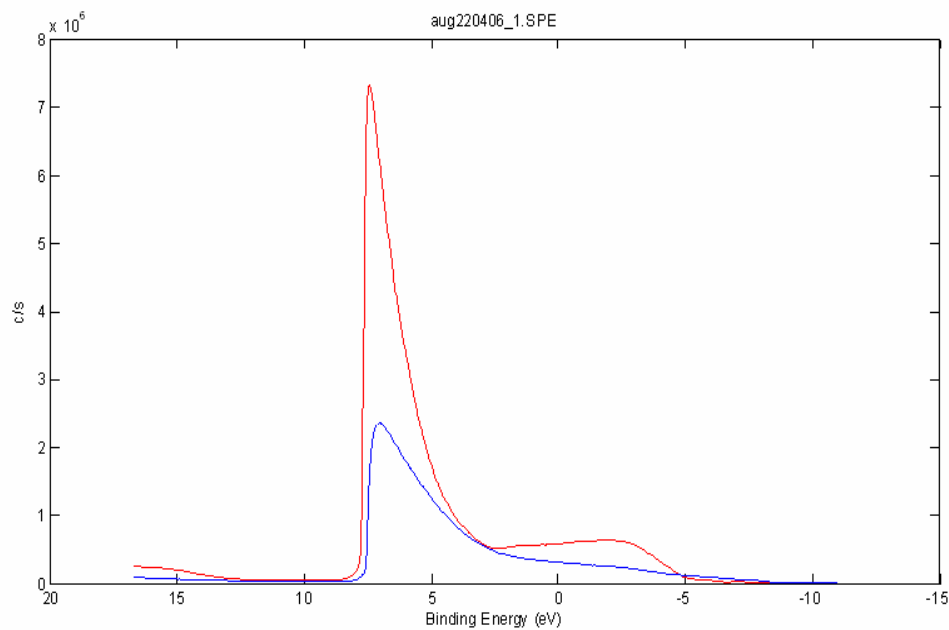
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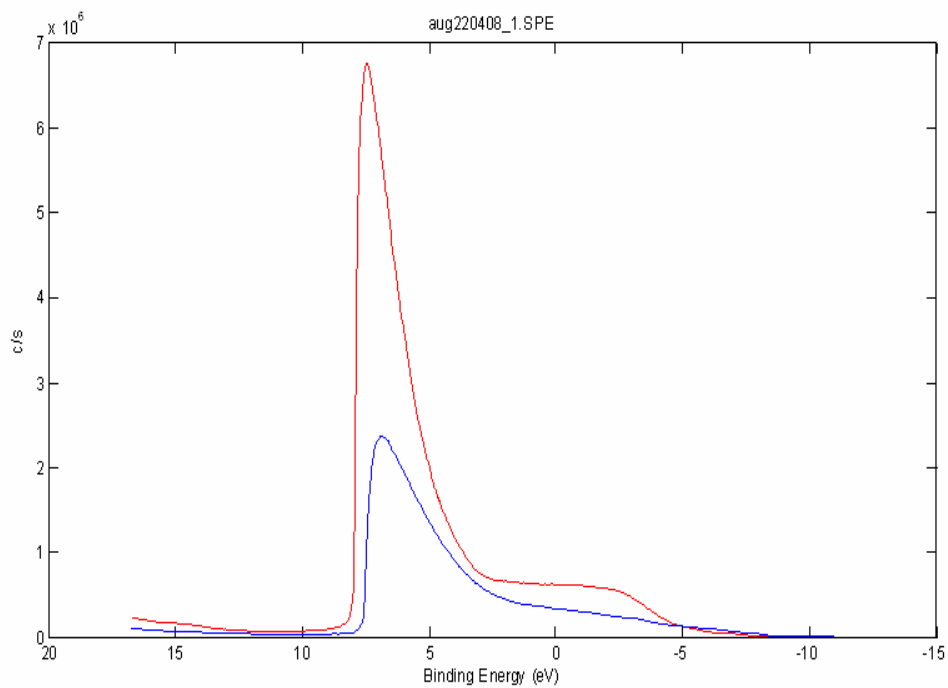


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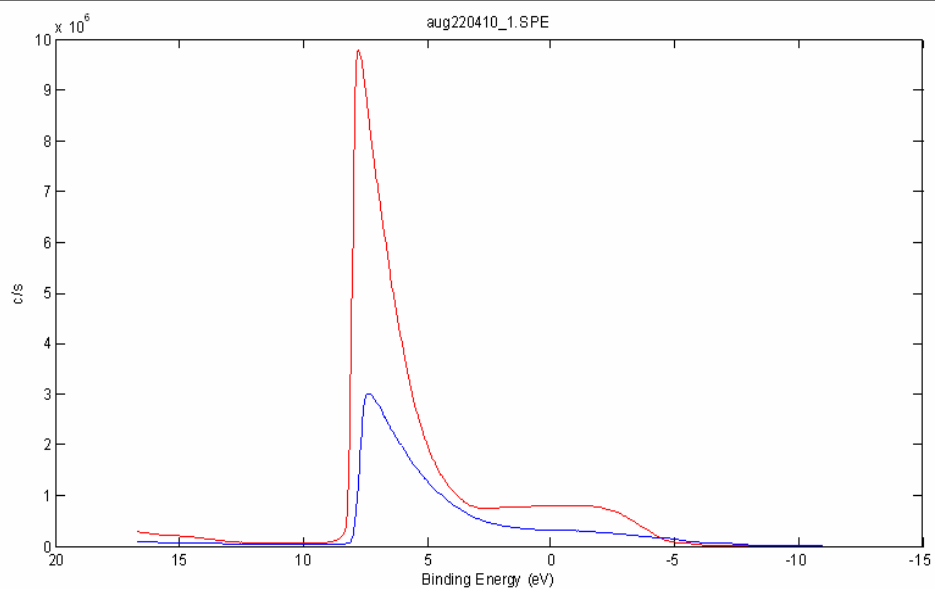
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(f)

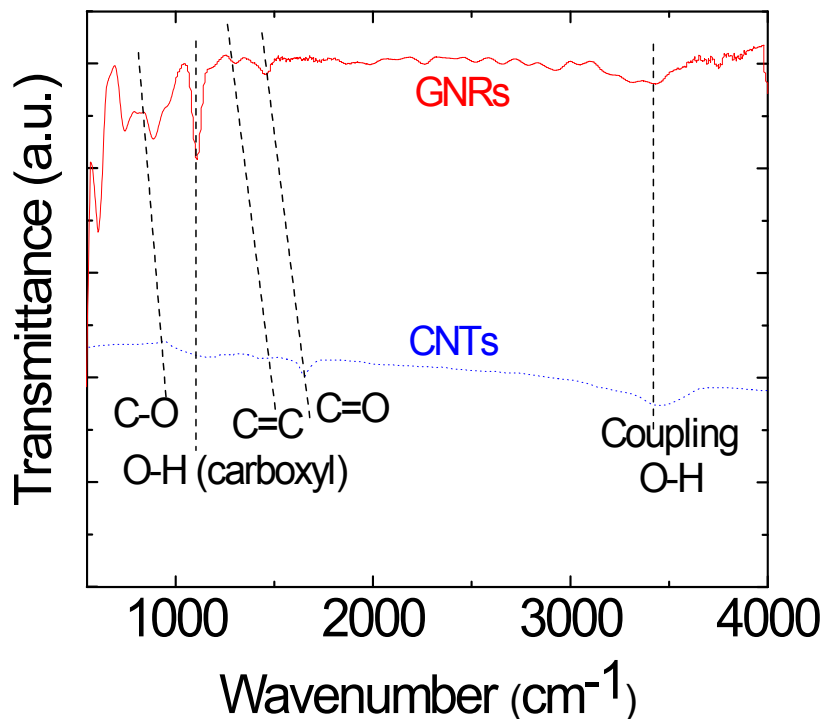
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**Figure S1.** UPS spectra of (a) GNRs, (b) CNTs, (c) PTB7:PC<sub>71</sub>BM, (d) PTB7:PC<sub>71</sub>BM/PEDOT:PSS, (e) PTB7:PC<sub>71</sub>BM/MoO<sub>3</sub>/GNRs, and (f)

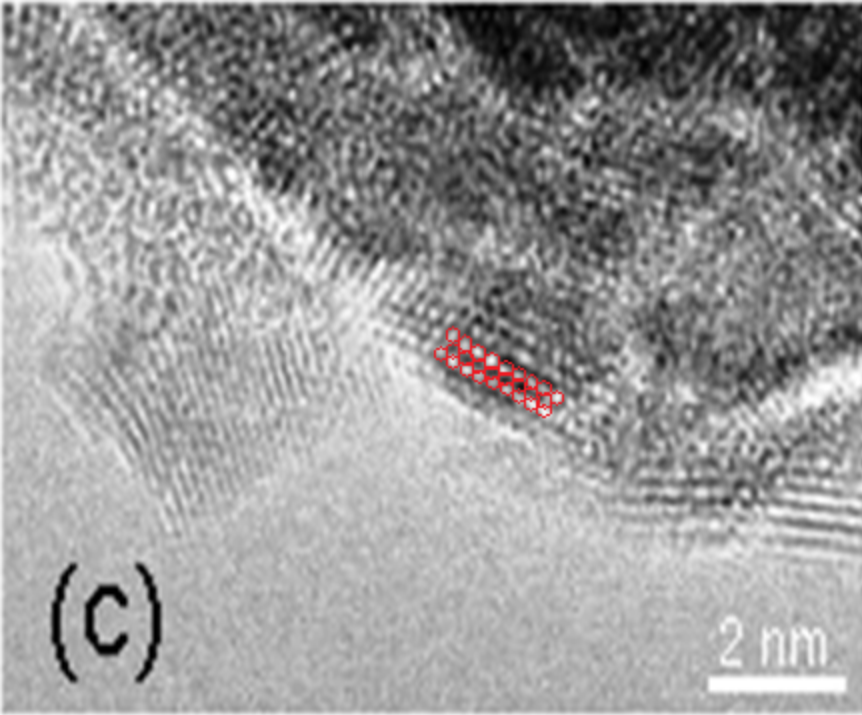
PTB7:PC<sub>71</sub>BM/CNTs/GNRs layers. The blue color line is the reference substrate while the red color line is the real sample.

The UPS spectra were obtained using HeI irradiation with  $h\nu=21.23$  eV produced by a UV source. During UPS measurements the analyzer was working at the Constant Retarding Ratio (CRR), with CRR of 10. The work function was determined from the UPS spectra by subtracting their width from the HeI excitation energy. Figure S1 demonstrates the UPS spectra with different onset values.



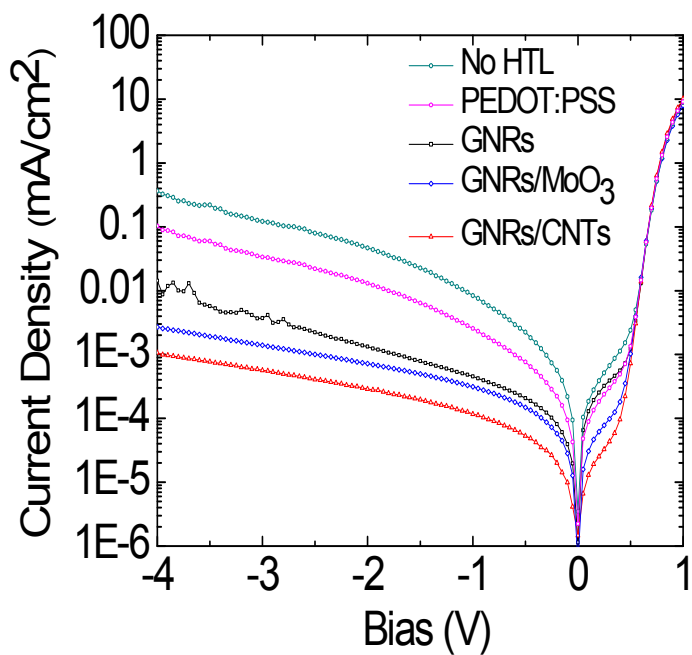
**Figure S2.** FTIR spectra of pristine CNTs and GNRs.

Figure S2 demonstrates clear differences between the pristine CNT and pristine GNRs.



**Figure S3.** The zoom in HR-TEM image from Figure 3c.

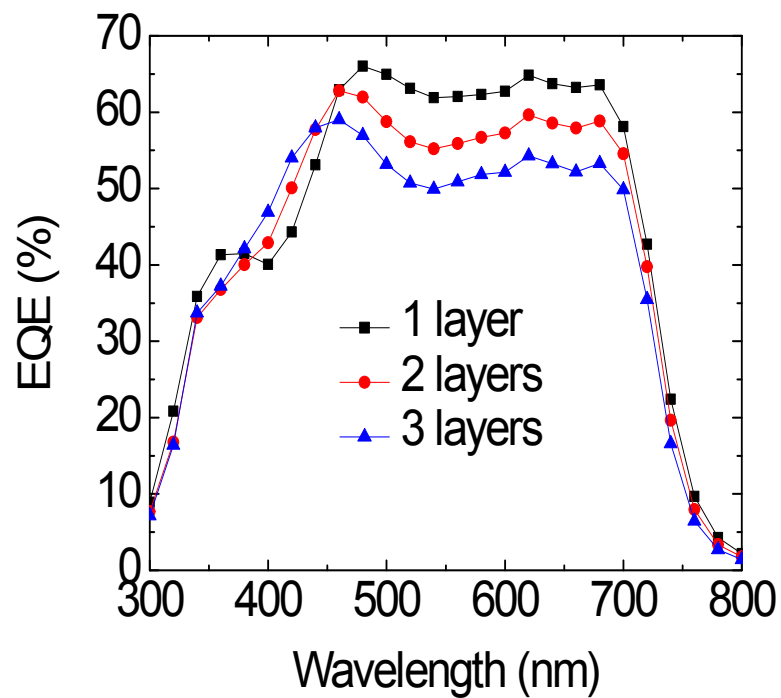
Figure S3 displays the zoom in HR-TEM image obtained from Figure 3c showing the zigzag configuration of our graphene nanoribbons.



**Figure S4.** Dark current-voltage plots of OPVs with various HTLs.

Figure S4 shows the dark current-voltage plot of different OPVs with various HTLs.





**Figure S5.** EQE spectra for OPVs with various GNRs.

Figure S5 shows the EQE spectra for OPVs with various GNR layers. From this figure the highest EQE is from the OPV with 1 layer of GNRs.

**Table S1.** Photovoltaic parameters of GNRs-based organic photovoltaic with different HTLs.

HTL	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)
No HTL	-11.20±0.11	0.70±0.01	51.05±0.10	4.00±0.03
PEDOT:PSS	-16.18±0.10	0.76±0.01	59.56±0.11	7.32±0.04
CNTs	-11.23±0.07	0.69±0.01	57.19±0.04	4.45±0.10
GNRs	-13.74±0.02	0.74±0.01	56.14±0.02	5.88±0.10
GNRs/MoO <sub>3</sub>	-14.50±0.10	0.75±0.01	57.67±0.06	6.11±0.01
GNRs/CNTs	-15.79±0.02	0.75±0.01	63.84±0.01	7.60±0.01

**Table S2.** Photovoltaic parameters of the fabricated device with different GNRs layers.

GNRs	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF (%)	PCE (%)	$R_s$ ( $\Omega$ cm <sup>2</sup> )
1 layer	-15.79±0.02	0.75±0.01	63.84±0.01	7.60±0.01	14.22
2 layers	-12.42±0.11	0.73±0.01	56.86±0.13	5.14±0.04	26.13
3 layers	-11.20±0.02	0.70±0.01	56.68±0.11	4.44±0.11	26.04