Supporting Information

Graphene oxide/oxygen deficient molybdenum oxide nanosheets bilayer as a hole transport layer for efficient polymer solar cells

Shan Chen,[a] Xiaowen Yu,[a] Miao Zhang,[a] Jiamin Cao,[b] Yingru Li,[a] Liming Ding*[b] and Gaoquan Shi*[a]

[a]*Department of Chemistry, Tsinghua University, Beijing 100084, China*

[b]*National Center for Nanoscience and Technology, Beijing 100190, China*

*Corresponding author.

E-mail addresses: gshi@tsinghua.edu.cn (G. Shi), Ding@nanoctr.cn (L. Ding)

1. General characterization

UV-Vis absorption and transmission spectra were recorded on a Hitachi U-3010 spectrophotometer. Raman spectra were obtained on a Renishaw Raman microscope with a 532 nm laser. TEM was performed on a Hitachi H-7650 electron microscope operated at 80 kV. AFM was performed on a Dimension 3100 microscope (Veeco) in a tapping mode. XRD was carried out on a D8 Advanced X-ray diffractometer with Cu Kα radiation (Bruker). XPS spectra were recorded on an ESCALAB 250 photoelectron spectrometer (Thermofisher) with Al Kα (1486.6 eV) as the X-ray source. UPS spectra were taken out on an ESCALAB 250 photoelectron spectrometer (Thermofisher) with a He lamp. CV was conducted on a Shanghai Chenhua CHI620 voltammetric analyzer under argon in an anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A glassy-carbon electrode was used as the working electrode, a platinum-wire was used as the counter electrode, and an Ag/Ag^+ electrode was used as the reference electrode. All potentials were corrected against Fc/Fc^+. The GO film was dip-coated on the surface of a glassy-carbon electrode from its aqueous solution without post-treatment. The CV cycles for recording the oxidation and reduction waves were separately performed with a fresh GO film in the fresh electrolyte described above.

2. Preparation of MoO_{3-x} nanosheets and GO

MoO_{3-x} nanosheets were prepared according to the literature.[S1] 3 g MoO_3 powder (99%, China Rare Metal Material Co.) was ground with 2 mL N-methyl-2-pyrrolidone (NMP) for 1 h. Then the paste-like mixture was put into a vacuum oven at 60 °C to remove solvent. The powder was dispersed in a 1:1 (v/v) DI water/ethanol mixture (45 mL), probe-sonicated for 2 h, and then centrifugalized at 6,000 rpm for 30 min twice. The light-blue supernatant was collected and then irradiated under a solar simulator (~80 mW cm^{-2}) for 5 h. The dark-blue dispersion of MoO_{3-x} nanosheets in DI water/ethanol mixture was obtained with a concentration of ~5 mg mL^{-1}. GO was synthesized according to the literature.[S2]

3. Characterization of MoO_{3-x} nanosheets

The dispersion of MoO_{3-x} nanosheets has an absorption peak at 762 nm (Fig. S2a). Fig.

S2b shows Raman spectra of MoO_{3-x} nanosheets and bulk α-MoO_3. The spectrum of bulk α-MoO_3 shows peaks at 159, 285, 667, 820 and 996 cm^{-1}.[S3–S5] The spectrum of MoO_{3-x} nanosheets presents new peaks at 195, 354, 489 and 732 cm^{-1}, resulting from shortening of Mo-O bond.[S1] X-ray photoelectron spectroscopy (XPS) for Mo 3d was used to identify the stoichiometry of MoO_{3-x} nanosheets (Fig. S2c). Each XPS peak can be resolved into two peaks, corresponding to different oxidation states of molybdenum. Peaks at 235.8 and 232.7 eV are assigned to $3d_{3/2}$ and $3d_{5/2}$ electrons of Mo^{6+}, respectively. Peaks at 234.9 and 231.7 eV are assigned to $3d_{3/2}$ and $3d_{5/2}$ electrons of Mo^{5+}, respectively. XRD pattern of MoO_{3-x} nanosheets presents similar peaks to those of bulk α-MoO_3, but they are weaker and broader because of structural defects and much thinner thicknesses (Fig. S3).

4. Device fabrication and measurements

Patterned ITO glasses with a sheet resistance of 15 Ω sq^{-1} were ultrasonically cleaned using detergent, distilled water, acetone, and isopropanol sequentially, and followed by a UV-Ozone treatment. For PEDOT:PSS cells, the aqueous dispersion of PEDOT:PSS (Clevios™ P VP Al 4083) was spin-coated (4,000 rpm for 30 s) onto ITO glass. The films were annealed at 150°C for 10 min in air. For MoO_{3-x} cells, the dispersion of MoO_{3-x} nanosheets (2 mg mL^{-1}) in 1:1 (v/v) DI water/ethanol mixture was spin-coated (3000 rpm for 30 s) onto ITO glass. For GO/MoO_{3-x} cells, the aqueous dispersion of GO (0.5 mg mL^{-1}) was firstly spin-coated (4000 rpm for 30 s) onto ITO glass. GO substrates stayed in air at room temperature for 20 min. Then, the dispersion of MoO_{3-x} nanosheets in DI water/ethanol mixture (2 mg mL^{-1}) was spin-coated (3000 rpm for 30 s) onto GO to form GO/MoO_{3-x} hole transport layer (HTL). A P3HT:$PC_{61}BM$ blend in *o*-dichlorobenzene (ODCB) (1:1 w/w, 34 mg mL^{-1}) was spin-coated (800 rpm for 30 s) onto different HTLs. The wet blend films were put into glass petri dishes to undergo solvent annealing. The active layer was annealed at 130 °C for 10 min in glove box. Finally, Ca (~10 nm) and Al (~100 nm) were thermally evaporated under a shadow mask (pressure ca. 10^{-4} Pa). The effective area for the cells is 4 mm^2. For PThBDTP:$PC_{71}BM$ cells, the fabrication process is similar to above, except active layer preparation: a PThBDTP:$PC_{71}BM$ blend in ODCB (1:1.2 w/w, 13 mg mL^{-1}) with 3 vol% 1,8-diiodooctane (DIO) was spin-coated (1200 rpm for 80 s) onto different HTLs.

J-V curves were measured by using a computerized Keithley 2420 SourceMeter.

The measurements were done in air under 100 mW cm^{-2} irradiation (calibrated with a NREL certified standard silicon cell) from a solar simulator (Newport, Model 91159A). EQE spectra were measured by a QE-R3011 measurement system (Enli Technology).

5. Supplementary tables

Table S1 Effects of MoO_{3-x} film thickness on the performances of ITO/MoO_{3-x}/P3HT:$PC_{61}BM$/Ca/Al solar cells

Concentration (mg mL^{-1})	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	R_s (Ω cm^2)	R_{sh} (Ω cm^2)
0.5	0.59	8.17	60	2.93 (2.74)	8.46	914.29
1	0.61	8.54	64	3.35 (3.13)	8.97	1176.81
2[a]	0.62	8.95	67	3.72 (3.61)	9.32	1355.03
3	0.62	9.26	62	3.56 (3.39)	12.18	1293.42

[a] The thickness is ~7 nm.

Table S2 Effects of annealing temperature of MoO_{3-x} films on the performances of ITO/MoO_{3-x}/P3HT:$PC_{61}BM$/Ca/Al solar cells

Temperature (°C)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	R_s (Ω cm^2)	R_{sh} (Ω cm^2)
without	0.62	8.95	67	3.72 (3.61)	9.32	1355.03
80	0.62	9.06	65	3.66 (3.52)	9.83	1282.35
150	0.62	9.27	64	3.69 (3.49)	10.02	1361.11
200	0.61	8.74	66	3.54 (3.41)	9.71	1480.43

Table S3 The onset potentials of the redox waves and energy levels of a GO film

E_{Ox1}^{onset}, [a] (V)	E_{Red1}^{onset}, [a] (V)	HOMO [b] (eV)	LUMO [b] (eV)
0.5	–1.6	–5.3	–3.2

[a] Potential in volt vs Fc/Fc^+. [b] The HOMO and LUMO energy levels of GO were calculated according to empirical formulas: HOMO = $-(E_{Ox1}^{onset} + 4.8)$ eV, LUMO = $-(E_{Red1}^{onset} + 4.8)$ eV.

6. Supplementary figures

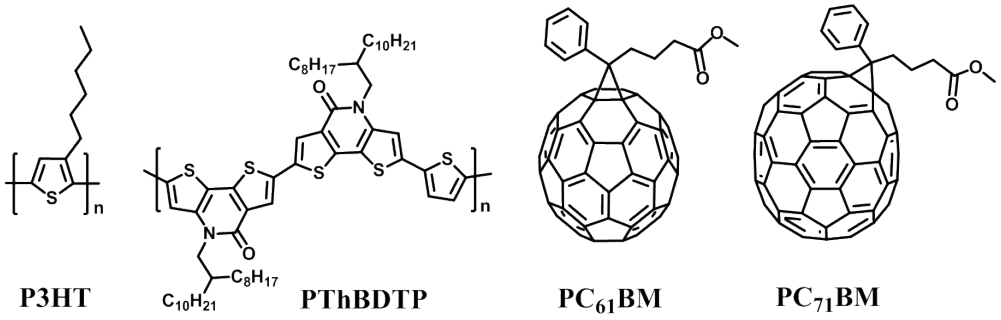

Fig. S1 Chemical structures of P3HT, PThBDTP, $PC_{61}BM$ and $PC_{71}BM$.

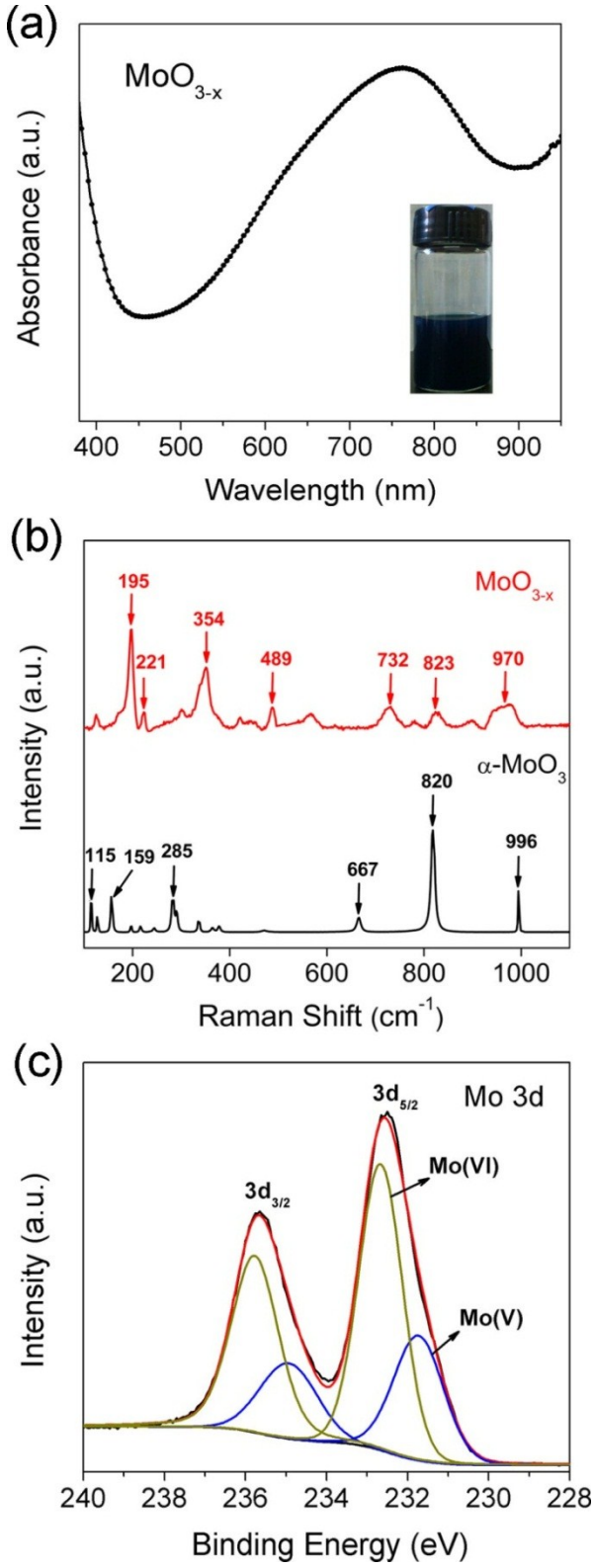

Fig. S2 (a) UV/Vis absorption spectrum of MoO_{3-x} nanosheets dispersed in a water/ethanol mixture (1:1, by volume). Inset: a photograph of this dispersion. (b) Raman spectra of MoO_{3-x} nanosheets and α-MoO_3. (c) XPS spectrum of MoO_{3-x} nanosheets.

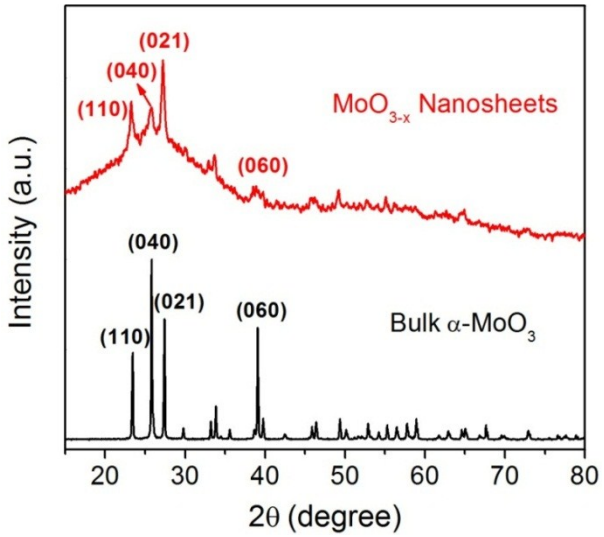

Fig. S3 XRD patterns of MoO_{3-x} nanosheets and α-MoO_3.

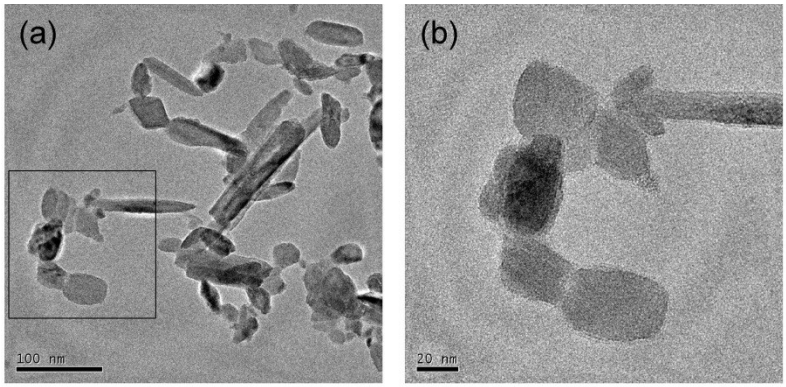

Fig. S4 TEM images of MoO_{3-x} nanosheets with different magnifications.

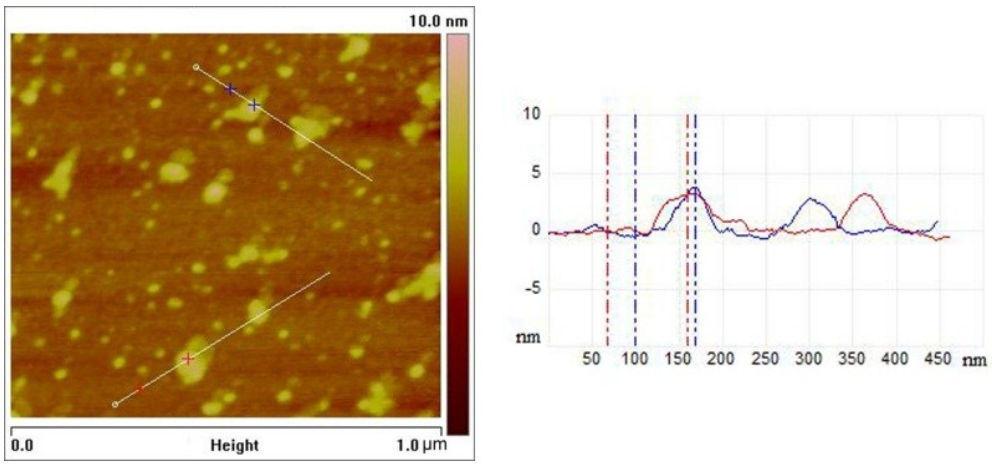

Fig. S5 AFM image of MoO_{3-x} nanosheets.

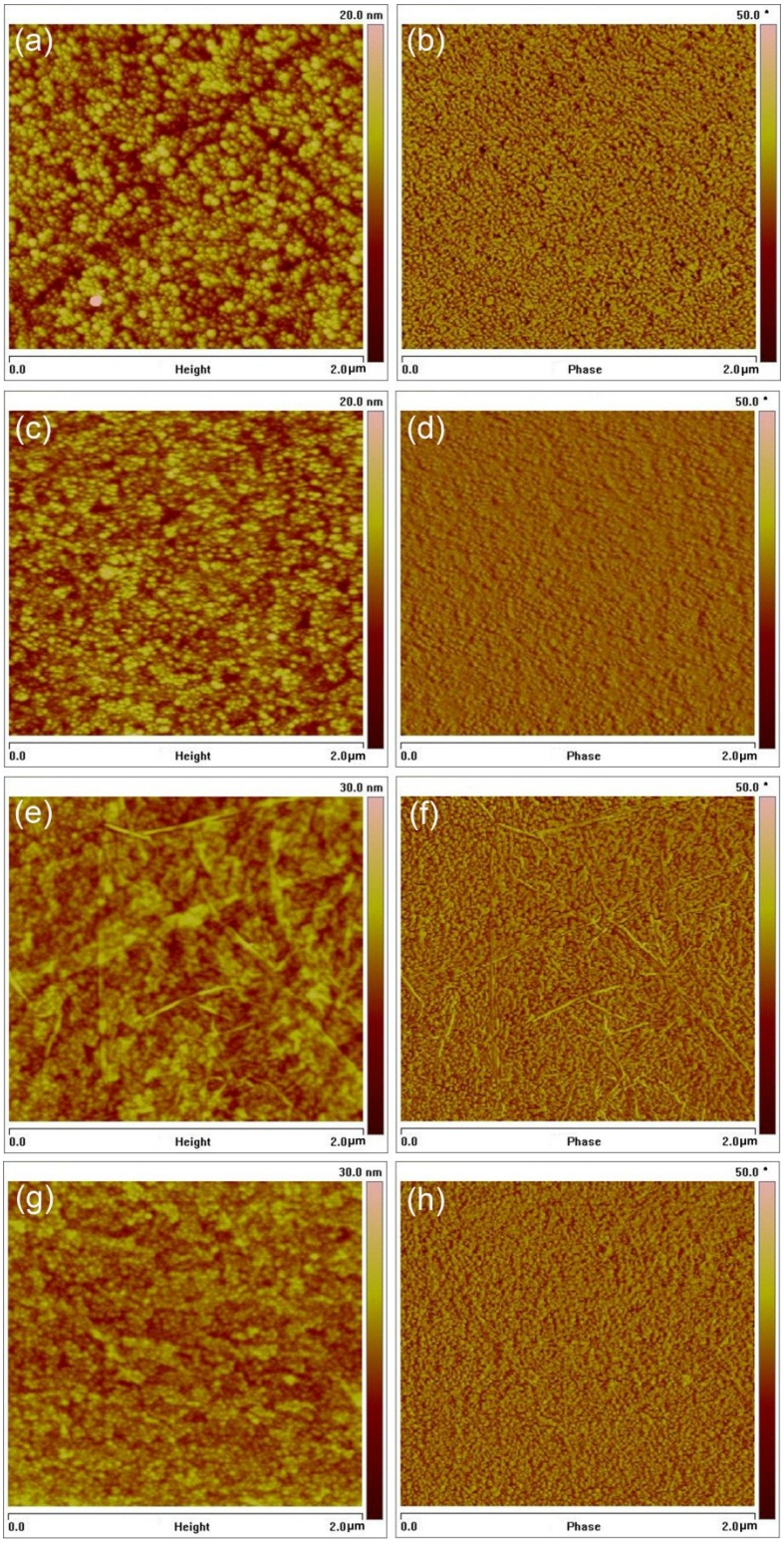

Fig. S6 AFM height (left) and phase (right) images of ITO glass surface before (a, b) and after coating with MoO_{3-x} (c, d), GO (e, f) and GO/MoO_{3-x} (g, h) films, respectively.

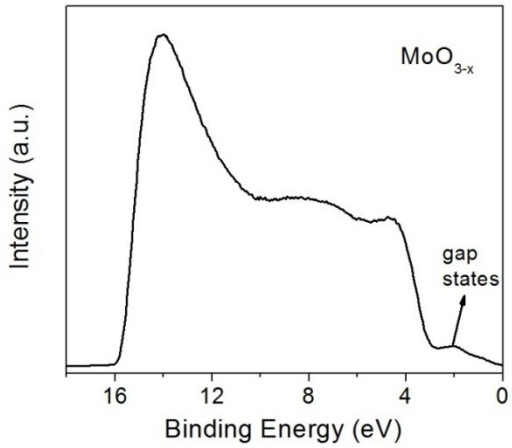

Fig. S7 UPS spectrum for MoO_{3-x} film.

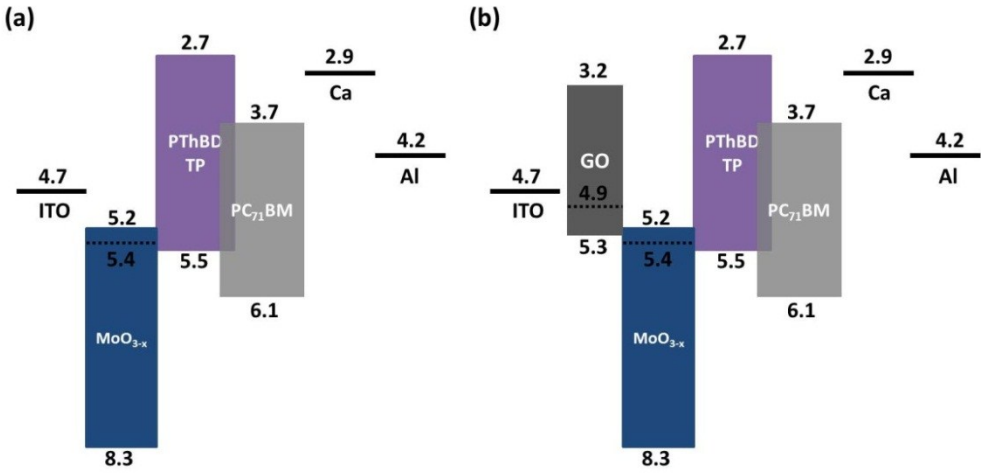

Fig. S8 Energy level diagrams (eV) of (a) ITO/MoO_{3-x}/PThBDTP:$PC_{71}BM$/Ca/Al and (b) ITO/GO/MoO_{3-x}/PThBDTP:$PC_{71}BM$/Ca/Al solar cells.

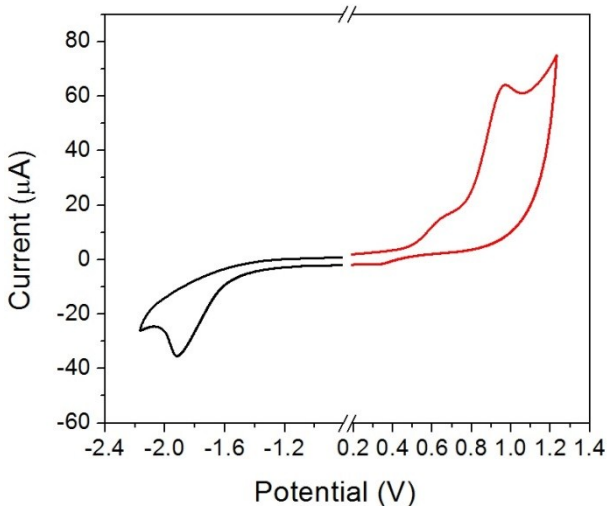

Fig. S9 Cyclic voltammogram of a GO film in anhydrous CH_3CN solution with $TBAPF_6$ (0.1 M) at a scan rate of 100 mV/s.

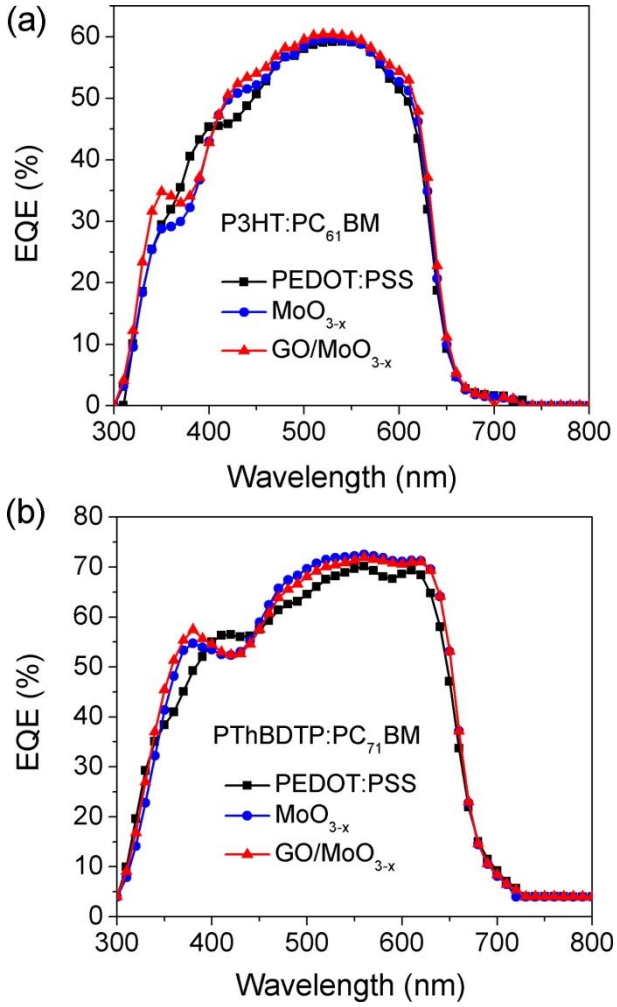

Fig. S10 EQE spectra of (a) P3HT:$PC_{61}BM$ and (b) PThBDTP:$PC_{71}BM$ solar cells with PEDOT:PSS, MoO_{3-x} or GO/MoO_{3-x} HTLs, respectively.

Supplementary references

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