

## **Efficacy Beyond 17% *via* Engineering the Length and Quality of Grafts in Organic Halide Perovskite/CNT Photovoltaics**

Samira Agbolaghi<sup>a,1</sup>

<sup>a</sup>Chemical Engineering Department, Faculty of Engineering, Azarbaijan Shahid  
Madani University, P.O. BOX: 5375171379, Tabriz, Iran

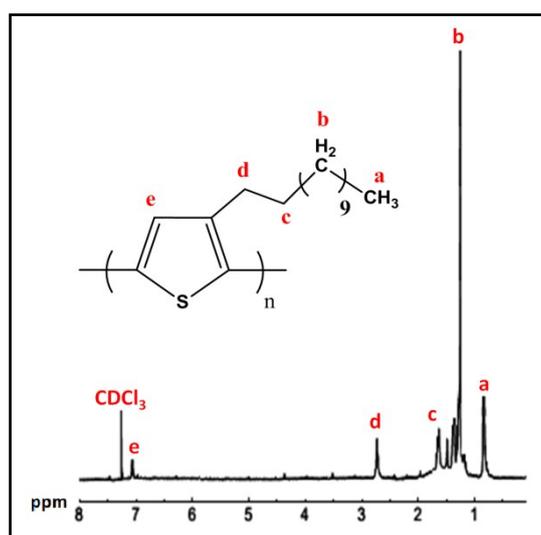
### **Experimental**

**Synthesis of CNTs-g-PDDT.** A 100 mL flask equipped with a condenser, dropping funnel, gas inlet/outlet and a magnetic stirrer was charged with CNTs-COOH-*f*-HMTh (0.5 g) and dried CHCl<sub>3</sub> (30 mL), and then was sonicated with a bath type sonicator for 40 min to reach a homogeneous suspension. Hereafter, 3-dodecylthiophene monomer (1.5 g) was added and the reaction mixture was deaerated by bubbling highly pure argon for 5 min. In a parallel system, 5 g of anhydrous ferric chloride was dissolved in 20 mL of dried acetonitrile. This solution was also deaerated and then slowly added to the reaction mixture at a rate of 5 mL min<sup>-1</sup> under an argon atmosphere. The reaction mixture was refluxed for about 24 h at room temperature under an inert atmosphere. The reaction was terminated by pouring the flask content into a large amount of methanol. The product was filtered and washed several times with methanol. The dark color solid was dried in vacuum at room temperature. The crude product was extracted with CHCl<sub>3</sub> in a Soxhlet for 24 h to remove pure poly(3-dodecyl thiophene). The polymer solution was filtered, precipitated into excess methanol, and dried in reduced pressure to reach a dark color powder. <sup>1</sup>HNMR spectra of PDDT oligomer is also represented in Fig. S1(a). FT-IR spectrum of CNTs, carboxylated carbon nanotubes, and thiophene functionalized/grafted carbon nanotubes are reported in Fig. S1(b). In FT-IR

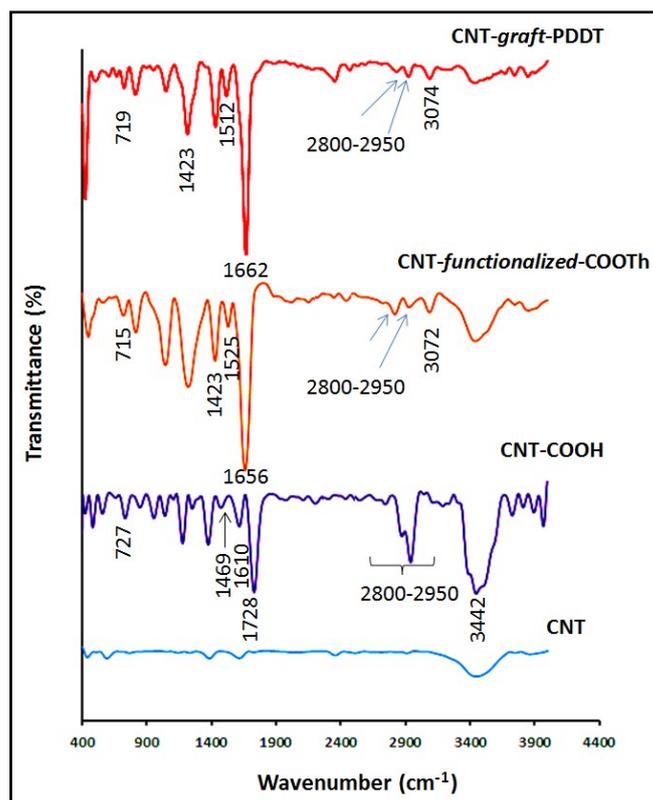
---

<sup>1</sup> Corresponding author (E-mail address): s.agbolaghi@azaruniv.ac.ir

spectrum of CNT-COOH, the stretching vibration absorbance of C=O in carboxylic acid appeared at  $1728\text{ cm}^{-1}$  and a broad peak centered at  $3442\text{ cm}^{-1}$  was detected as characteristic of an O–H stretch due to alcoholic or phenolic or carboxylic groups (Fig. S1(b)). In FT-IR spectrum of the thiophene functionalized carbon nanotubes, the vibrational peaks originating from the stretching of C–S and C=O were observed at around  $715$  and  $1656\text{ cm}^{-1}$ , respectively. The most important bands in FT-IR spectrum of CNT-g-PDDT were the weak aromatic  $\alpha$  and  $\beta$  hydrogens of thiophene rings at  $3000\text{--}3100\text{ cm}^{-1}$ ,  $\gamma(\text{C–H})$  in the aromatic ring at  $719\text{ cm}^{-1}$ , the aromatic C=C stretching vibration at  $1423$ ,  $1512\text{ cm}^{-1}$  and C–S stretching vibration in thiophene rings at  $702\text{ cm}^{-1}$ . Further vibration from the CH-aliphatic bonds could be detected at around  $2800\text{--}2950\text{ cm}^{-1}$ . FT-IR spectra assignments verified that the MWCNTs had been successfully oxidized into the shorter carboxylated carbon nanotubes (CNT–COOH) and after which, thiophene groups were successfully introduced into the carbon nanotubes (CNT-*functionalized*-COOTh). After graft polymerization of thiophene derivatives onto functionalized CNTs, an increase was observed in the intensity of bands related to the polythiophene derivatives; however, the intensity of peaks attributed to MWCNTs decreased due to their low concentration in the grafted hybrid.



(a)



(b)

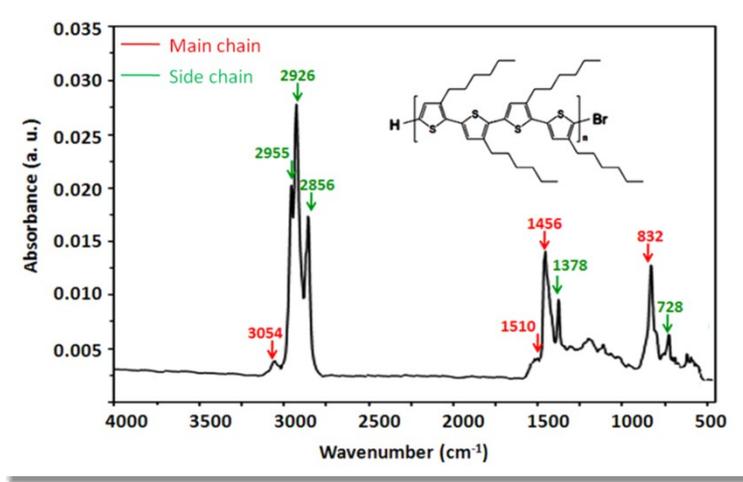
**Fig. S1.**  $^1\text{H}$ NMR spectra of PDDT oligomer (a); FT-IR spectra of CNT, CNT-COOH, functionalized and grafted CNT with PDDT.

**Carboxylated carbon nanotubes (CNT-COOH).** Functionalization of CNTs was carried out via oxidation method with sonication of sulfuric acid (15 mL, 95–97%) and nitric acid (45 mL, 65 %) having a ratio of 1:3 v/v for 6 h at 50 °C. A five-fold dilution was then applied to the mixture for stopping the oxidation reaction. Stirring and decantation were performed for five times and finally washed with deionized water by filtration until the water pH reached 7. The precipitate was finally dried in vacuum oven at 60 °C. The CNT-COOH with high oxidation was synthesized by the same procedure for 9 h at 60 °C.

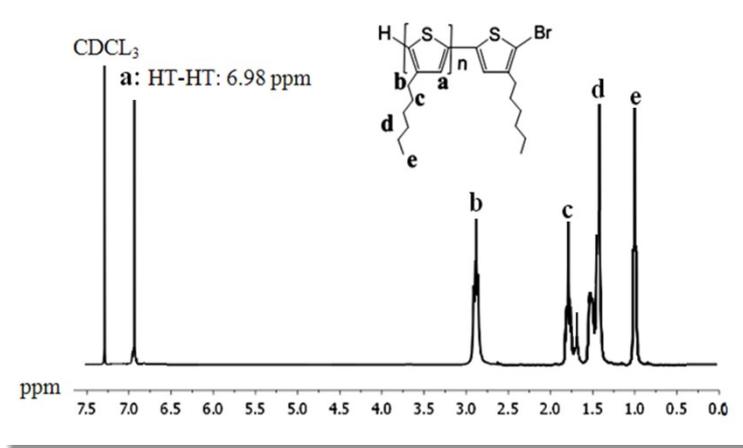
**Thiophene functionalized carbon nanotubes (CNT-functionalized-COOTH).** The 2-hydroxymethyl thiophene (CNT-COOH-functionalized-HMTh) macroinitiator was synthesized by the esterification of CNT-COOH with 2-hydroxymethyl thiophene in the

presence of *p*-TSA as a dehydrating agent (5 wt% of acid). In brief, a three-neck flask equipped with a dean-stark trap, gas inlet/outlet, and a magnetic stirrer was charged with CNT-COOH (0.5 g), 2-hydroxymethyl thiophene (1 g) and anhydrous dimethyl sulfoxide (50 mL), and then was sonicated with a bath type sonicator for 40 min to produce a homogeneous suspension. A catalytic amount of *p*-TSA as a dehydrating agent was added to the flask, and the reaction mixture was de-aerated by bubbling highly pure argon for 10 min. Thereafter, the flask was placed in a silicon oil bath at 140 °C and the reaction mixture was stirred for 6 h under argon atmosphere. The reaction water was removed as an azeotrope until no more water was formed. The suspension was then centrifuged and washed several times with methanol for remove of remaining 2-hydroxymethyl thiophene. The CNT-COOH-*f*-HMTh powder was obtained after drying in reduced pressure at 60 °C. The CNT-COOH-*f*-HMTh macromonomer with a high density of thiophenic adducts was also prepared by the same procedure and with appropriate amounts of CNT-COOH (high density) (0.5 g) and 2-hydroxymethyl thiophene (2 g).

**Synthesis of CNT-*g*-P3HT.** The regioregular P3HTs (RR-P3HT, > 99%) with the molecular weights ( $M_n$ ) of 5 and 50 kDa and the dispersities of 1.18 and 1.19 were synthesized through Grignard metathesis polymerization [1]. FT-IR and <sup>1</sup>HNMR spectra of P3HT<sub>50000</sub> are reported in Fig. S2. The end functionalization of P3HT was carried out according to the reported procedure to yield CH<sub>2</sub>OH end groups [2]. The functionalization of CNTs was performed with reflux in 1:3 v/v mixture of sulfuric acid (95–97%) and nitric acid (65%) at 100 °C for 6 h to introduce the functional carboxyl acid groups. The CNT–COOH was reacted with SOCl<sub>2</sub> to acquire the acyl-chloride functionalized CNT. A condensation reaction was subsequently performed between the CH<sub>2</sub>OH-terminated P3HT and the acyl-chloride functionalized CNT to yield the CNT-*g*-P3HT (Fig. S3).

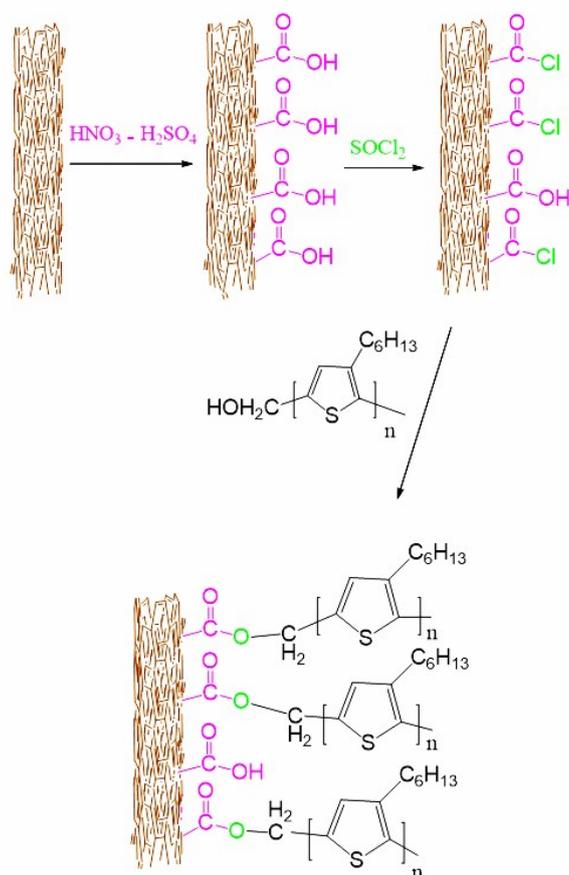


(a)



(b)

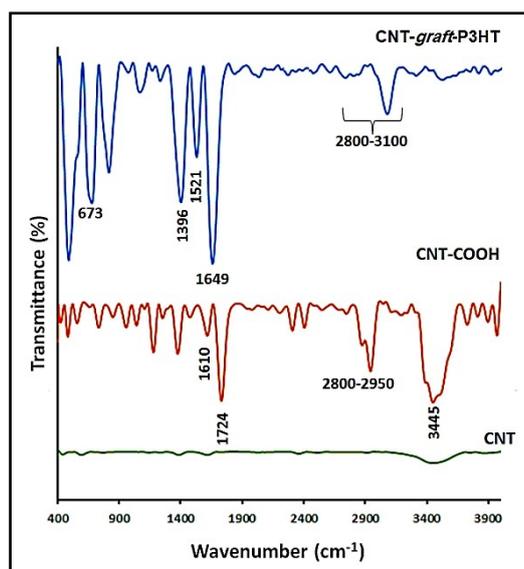
**Fig. S2.** FT-IR (a) and <sup>1</sup>H NMR (b) spectra of synthesized P3HT<sub>50000</sub>.



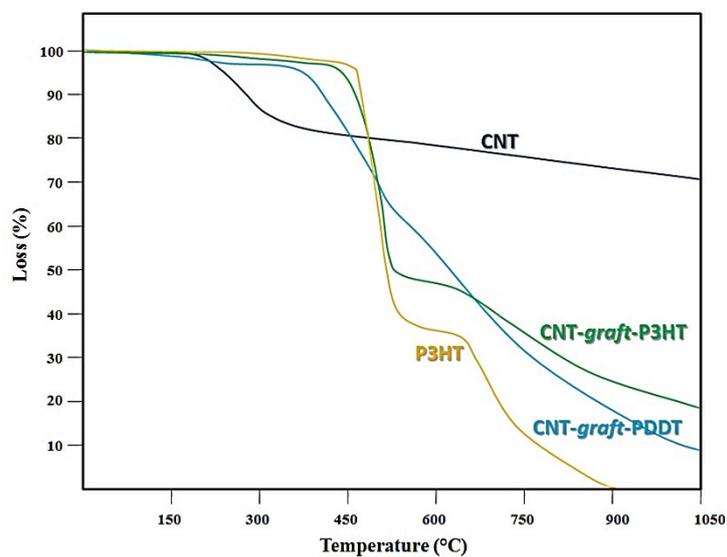
**Fig. S3.** Grafting of RR-P3HT chains onto the CNT surface to reach CNT-g-P3HT.

FT-IR spectrum of CNTs, carboxylated CNT, and P3HT-grafted MWCNT are shown in Fig. S4(a). In FT-IR spectrum of CNT-COOH, the stretching vibration absorbance of C=O in carboxylic acid appeared at  $1724\text{ cm}^{-1}$  and a broad peak at approximately  $3445\text{ cm}^{-1}$  characteristic of O-H stretch was observed due to alcoholic or phenolic or carboxylic groups. In FT-IR spectrum of CNT-g-P3HT, the vibrational peaks arising from the stretching of C-S and C=O related to the ester linkages appeared at around  $673$  and  $1649\text{ cm}^{-1}$ , respectively. Further vibration from the aromatic and aliphatic C-H bonds can be seen at around  $2800\text{--}3100\text{ cm}^{-1}$ . These FT-IR spectra assignments verified that the CNTs were successfully oxidized into the CNTs-COOH and after which, the P3HT chains were successfully grafted onto CNTs (CNT-g-P3HT).

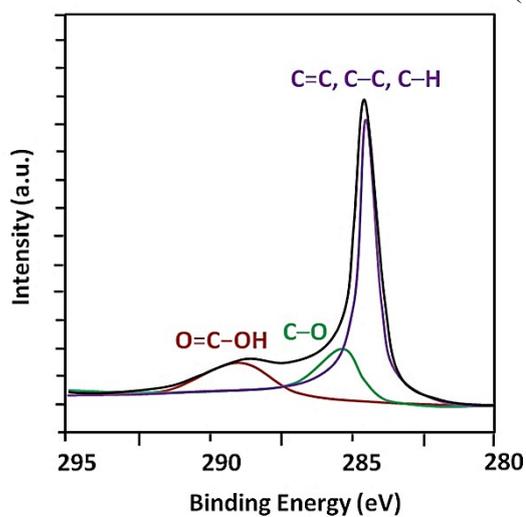
Fig. S4(b) reports the thermogravimetric analysis (TGA) results of CNT, P3HT, CNT-g-PDDT and CNT-g-P3HT samples. The residual contents at 1000 °C for the CNT and pure P3HT were 70 and 0%, respectively. At the same temperature, the residual contents of CNT-g-PDDT and CNT-g-P3HT samples were 10 and 20%, respectively (Fig. S4(b)). These grafted samples possessed at least 10 and 20% CNT in their structure. The thermal degradation onsets for the pure P3HT and CNT-g-P3HT samples were 460 and 443 °C, respectively, indicating the lower thermal stability of CNT-g-P3HT with respect to the pure P3HT. A decrease in thermal stability of CNT-g-P3HT compared to the pure P3HT could be originated from the oxygen species associated with the esteric linkage onto the CNT surface, which initiated the P3HT thermal degradation covalently bonded onto CNTs. In addition, the thermal degradation of CNT-g-PDDT was detected at a lower temperature (= 365 °C) compared to the CNT-g-P3HT (= 443 °C), demonstrating the lower thermal stability of former sample. The TGA analysis perfectly proved the grafting of P3HT and PDDT onto the CN surface. Fig. S4(c) shows the high-resolution XPS C 1s spectrum for the CNT-COOH, exhibiting the presence of O=C-OH (289.2 eV), C-O (285.5 eV), and C=C/C-C (284.6 eV). Fig. S4(d) shows the high-resolution XPS C 1s spectrum for CNT-g-P3HT. Compared with Fig. S4(c), Fig. S4(d) shows a dramatic decrease in the peak component at 289 eV, indicating the occurrence of the reactions. The peak components over 285–289 eV are still observable in Fig. S4(d), though not very well resolved due to the very low percentage of C-O and C=O bonds in the ester linkage in CNT-g-P3HT.



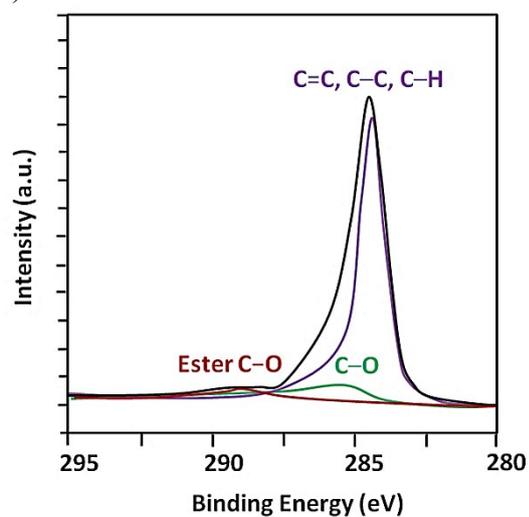
(a)



(b)

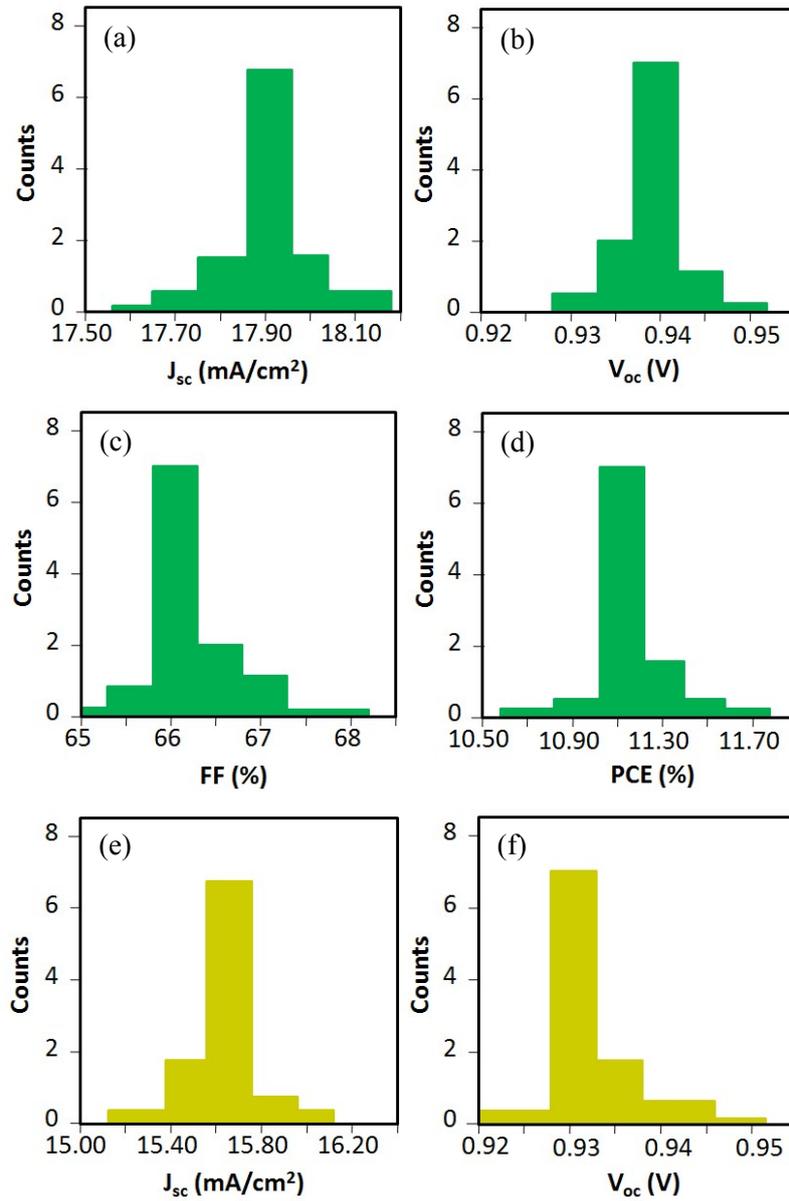


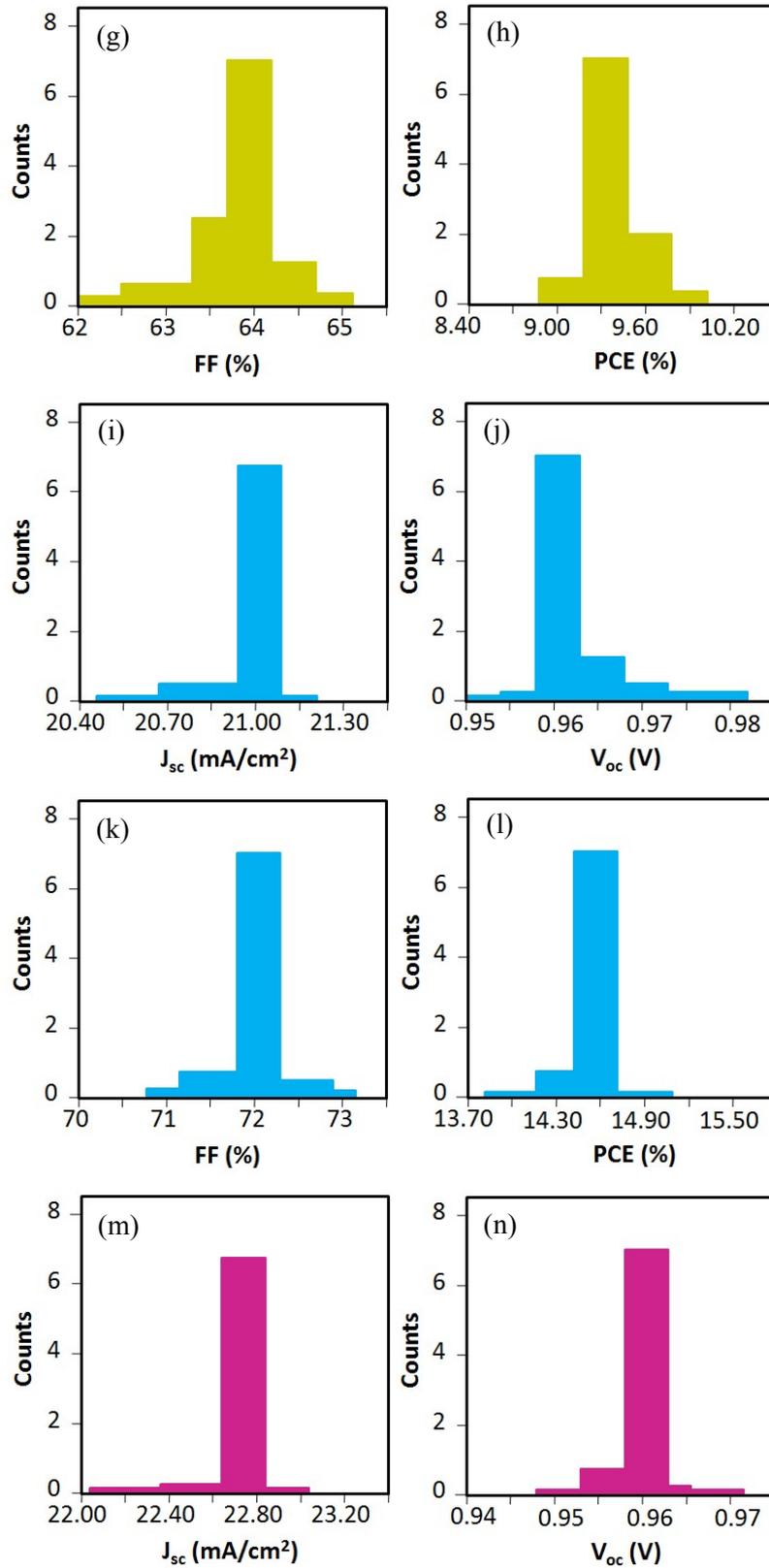
(c)

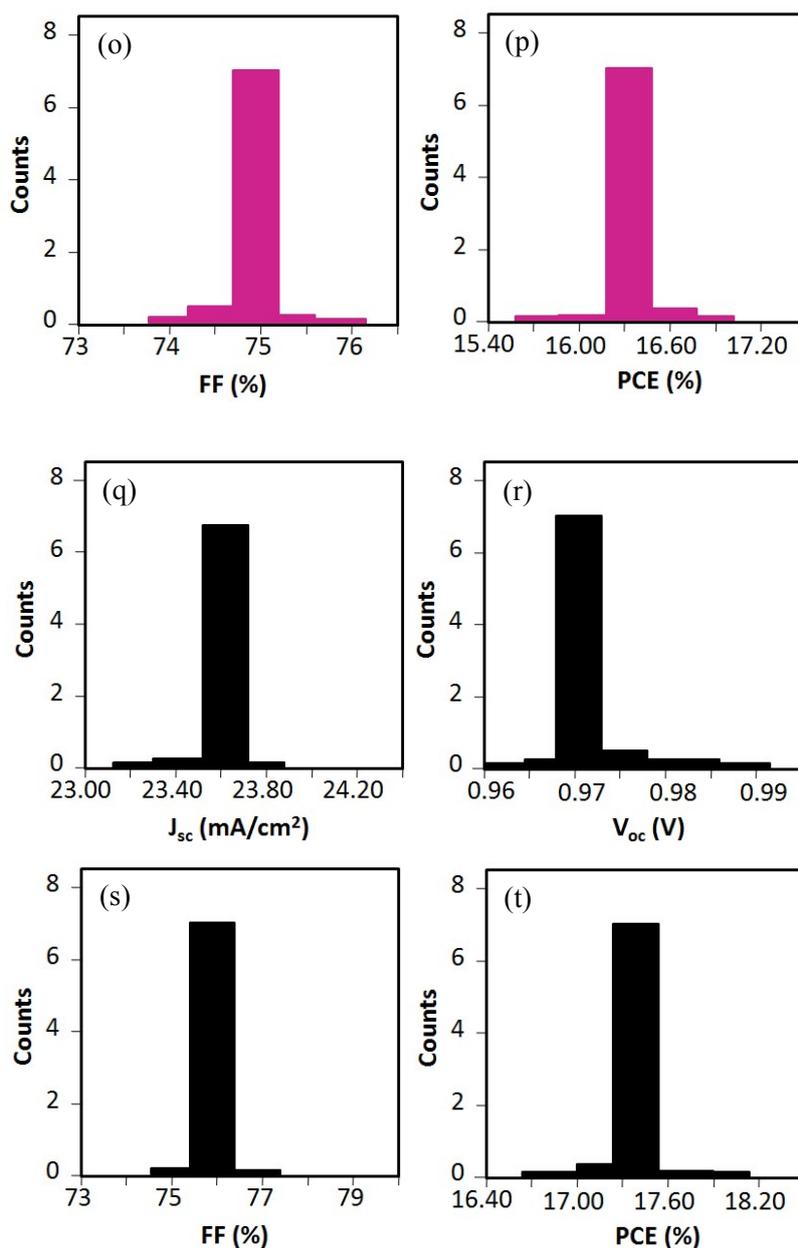


(d)

**Fig. S4.** FT-IR spectra of different utilized materials (a); TGA curves of CNT, P3HT, CNT-g-PDDT and CNT-g-P3HT (b); XPS spectra of surface modified CNT (c) and CNT-g-P3HT (d).  
(d).







**Fig. S5.** Histograms of photovoltaic characteristics for perovskite (a-d), perovskite + CNT (e-h), perovskite + CNT-g-PDDT (i-l), perovskite + CNT-g-P3HT (long) (m-p) and perovskite + CNT-g-P3HT (short) (q-t) solar cells.

### References

[1] Lohwasser, R.H. and Thelakkat, M., 2011. Toward perfect control of end groups and polydispersity in poly (3-hexylthiophene) via catalyst transfer polymerization. *Macromolecules*, 44(9), pp.3388-3397.

[2] Liu, J. and McCullough, R.D., 2002. End group modification of regioregular polythiophene through postpolymerization functionalization. *Macromolecules*, 35(27), pp.9882-9889.