Supporting Information

Soluble P3HT-Grafted Graphene for Efficient Bilayer-heterojunction Photovoltaic Devices

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Experimental Details

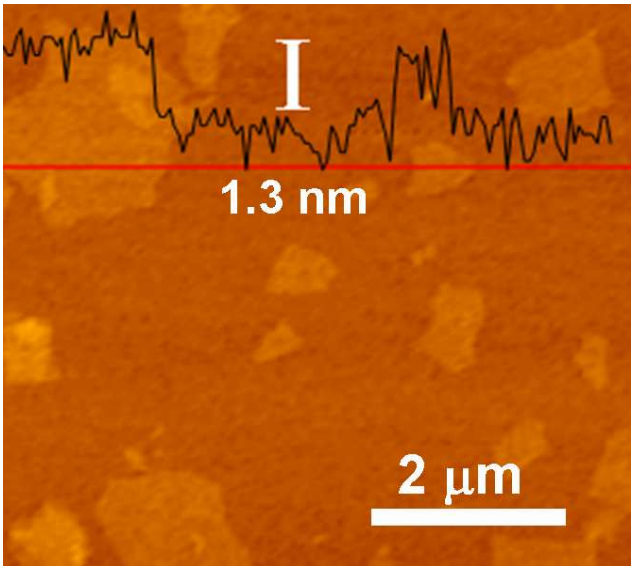
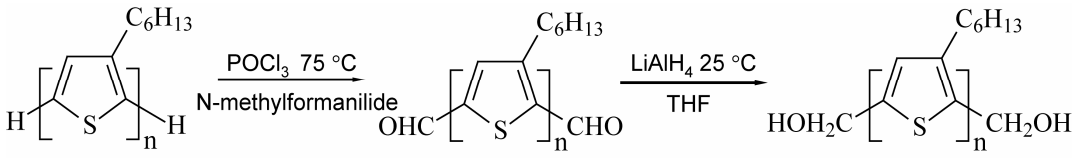


Figure S1. AFM image of individual GO sheets, showing a thickness of 1.3 nm.

Preparation of regioregular P3HT with –CH_2OH end groups



Scheme S1. The synthesis steps for regioregular P3HT with –CH_2OH end groups.[S1]

Scheme S1 illustrates the synthesis procedure for regioregular P3HT with –CH_2OH end groups.[S1] Firstly, formaldehyde groups (–CHO) were introduced on each end of the polymer chain. Typically, the commercially-available P3HT (0.3 g) was dissolved in anhydrous toluene (80 mL) under nitrogen protection. Thereafter, $POCl_3$ (1.3 mL, 0.014 mol) and *N*-Methylformanilide (2 mL, 0.016 mol) were successively added to the P3HT solution in toluene and kept at 75 °C for 24 hrs. The reaction mixture was then cooled down to room temperature, followed by the addition of saturated aqueous solution of sodium acetate (100 mL) and the mixture was stirred for another 2 hrs. The functionalized polymer was obtained by precipitating in methanol, followed by filtering and drying. Finally, the polymer with –CHO end groups was confirmed by NMR measurements. (Figure S2) According to literature information,[S1] the peaks at ~ ~10.02 and 9.96 ppm can be assigned to –CHO end groups.

The P3HT with –CHO end groups was then reduced with $LiAlH_4$ to yield a P3HT terminated by methylene hydroxyl groups (-CH_2OH). In a typical experiment,

regioregular P3HT with –CHO end groups (0.28 g) was dissolved in anhydrous THF (80 mL) under nitrogen protection. $LiAlH_4$ in THF (1.0 M, 1.0 mL) was then added. The mixture was kept stirring at room temperature for 40 min. Hydrochloric acid solution (1.0 M, 1.0 mL) was then added to quench the excess of $LiAlH_4$. The resultant functionalized polymer was purified by precipitating in methanol, followed by filtering and drying. The conversion of –CHO to $–CH_2OH$ in the polymer was confirmed by NMR analysis (Figure S3). The –CHO signals disappeared and new signals appeared at ~4.60 and 4.54 ppm, characteristic of the $–CH_2OH$ group.[S1] The NMR result of the resultant P3HT grafted graphene is also given in Figure S4. As can be seen, the signals assigned to –CHO and $–CH_2OH$ groups disappeared in the G-P3HT composite, confirming the reactions shown in Scheme 1S and Figure 1.

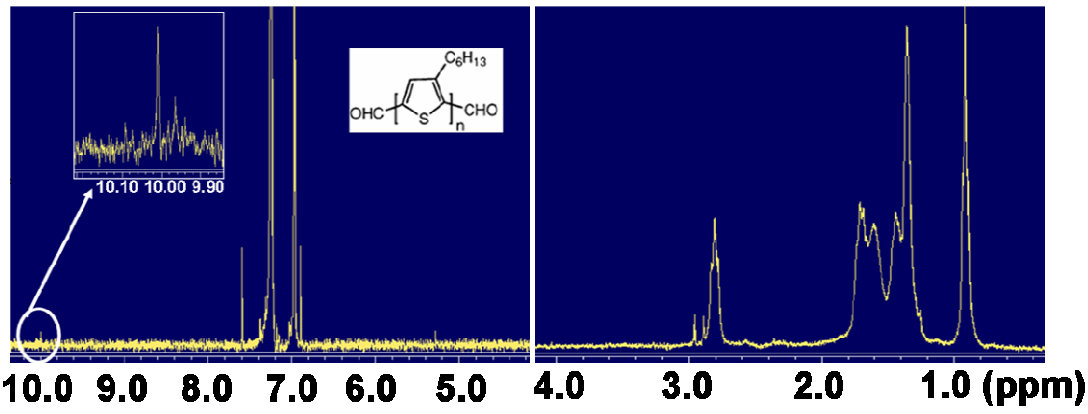


Figure S2. ^{1}H NMR spectrum of regioregular P3HT with –CHO end groups [^{1}H NMR ($CDCl_3$): 10.02-9.96 (2s, 2H totally), 6.96 (s, 56H), 2.79 (t, 120H), 1.62 (m, 112H), 1.42-1.36 (m, 340H), 0.9 (t, 170H)]

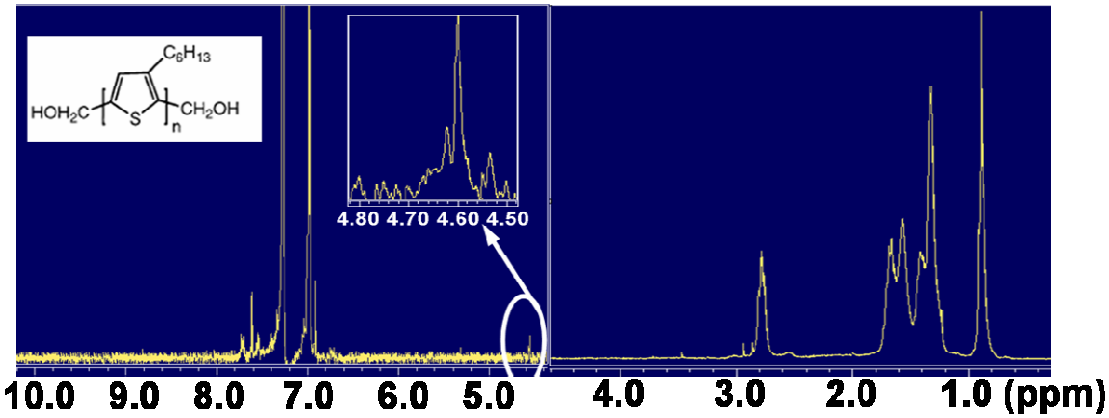


Figure S3. ^{1}H NMR spectrum of regioregular P3HT with –CH_2OH end groups. [^{1}H NMR ($CDCl_3$): 6.96 (s, 75H), 4.60-4.54 (2d, 4H totally), 2.79 (t, 150H), 1.62 (m, 150H), 1.42-1.36 (m, 450H), 0.9 (t, 225H)]

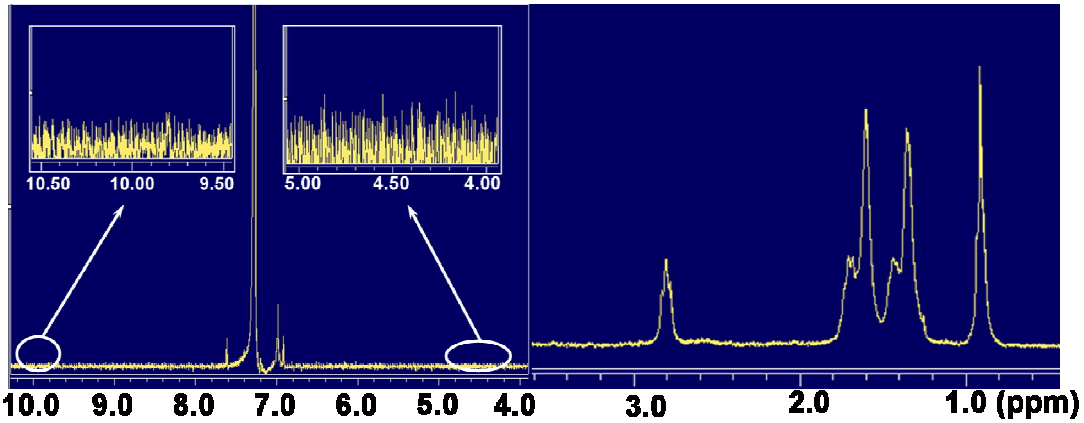


Figure S4. ^{1}H NMR spectrum of the P3HT-grafted graphene.

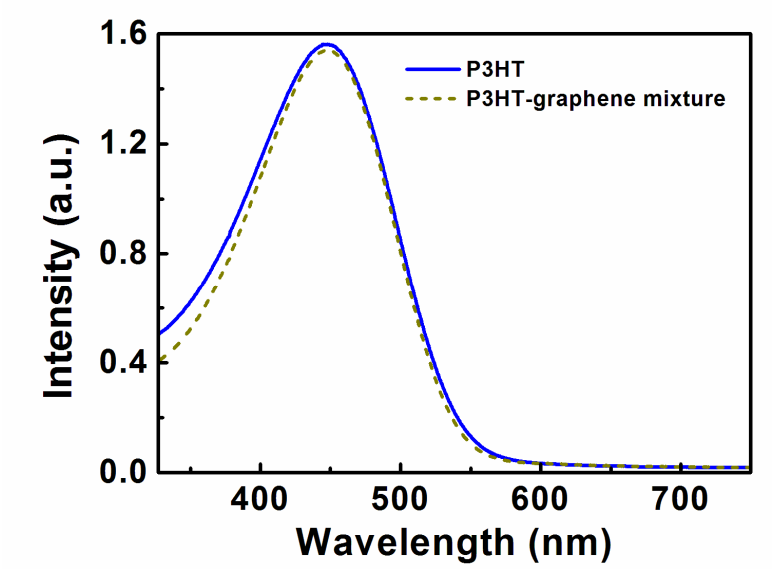


Figure S5. Absorption spectra of P3HT and the mixture of P3HT and graphene in chloroform.

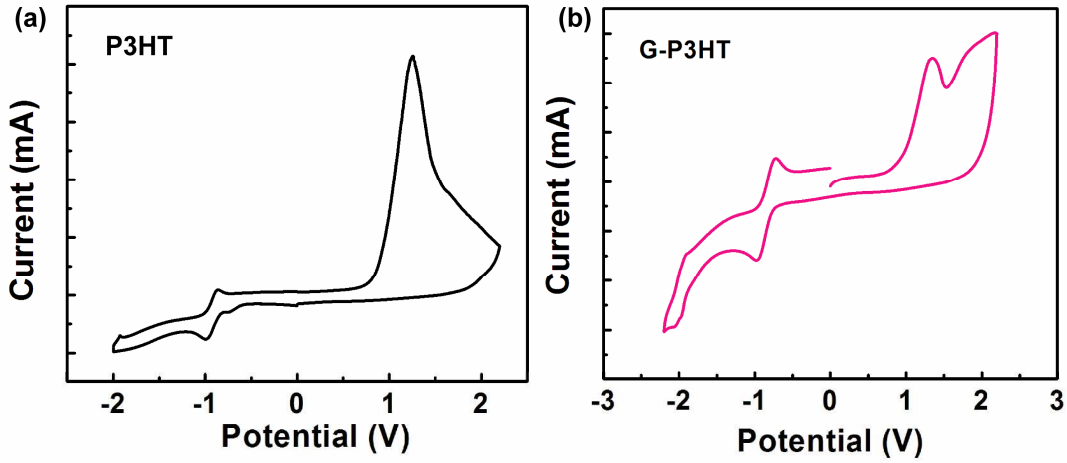


Figure S6. CV curves of thin films for (a) pure P3HT and (b) G-P3HT on glassy carbon electrodes.

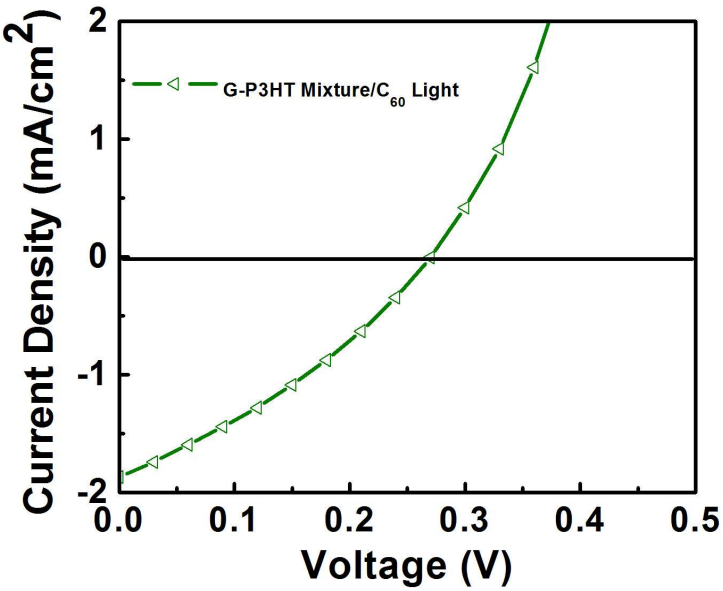


Figure S7. Current-voltage characteristic of the photovoltaic device based on the mixture of graphene and P3HT/C_{60}.

REFERENCES AND NOTES

S1. Liu, J.; McCullough, R. D. End Group Modification of Regioregular Polythiophene through Postpolymerization Functionalization. *Macromolecules* **2002**, *35*, 9882-9889.