



Journal Name

COMMUNICATION

Support information

Aggregation of P3HT as a preferred pathway for its chemical doping by F4-TCNQ

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Materials

Regioregular (rr) low molecular weight (LMW) P3HT (Mw=31.3 kDa, Mn=15.6kDa, H-T regioregularity = 93.6 %) was purchased from Ossila. Dopant F₄-TCNQ (>98%) was purchased from TCI America. The indium tin oxide (ITO) glass substrate was purchased from Colorado Concept Coating, LLC, USA and the glass slides was purchased from Fisher Scientific. The organic solvents in reagent grade were used as received.

UV-vis Sample Preparation.

A 1 mg/mL LMW P3HT in toluene solution was prepared by heating it at 90 °C until a transparent orange solution is formed. This stock solution was stable at room temperature over weeks. A 225 µg/mL F₄-TCNQ in toluene solution was also prepared. The P3HT solutions for UV-vis/UV-vis-NIR measurements were diluted from the stock solution by additions of appropriate amount of toluene, decane and dopant solution and transferred into air-sealed custom-made 2 mm cuvettes for UV-Vis and UV-Vis-NIR measurements. Decane fractions were in volume percentages. Doping ratio was calculated as (mass of F₄-TCNQ / mass of P3HT) x 100wt%. All preparations and handling of solution samples were carried out in a N₂ filled glovebox.

Film Sample preparation

ITO substrate was cleaned by ultrasonication for 15 mins in a mixture of 1:1:1 acetone/chlorobenzene/toluene solution. After sonication, it was blown dry under compressed ultrahigh-purity (>99.99%) N₂ flow.

For AFM measurements, LMW-P3HT was deposited by spin-coating 5 µL of 1 mg/mL LMW-P3HT stock solution on a 10x10 mm ITO substrate at 2000 rpm for 120s. The doped sample was obtained by dipping the as-deposited substrate in acetonitrile for 60 s and subsequently immersing the substrate into 225 µg/mL F₄-TCNQ in acetonitrile for 60 s. The undoped film sample was also dipped into acetonitrile solvent for 120 s as a control to eliminate the solvent effect. The partially dedoped sample was prepared by dipping the as-deposited substrate into 225 µg/mL F₄-TCNQ in acetonitrile for 60 s and subsequently rinsing in acetonitrile for 60 s. The prepared sample substrates were blown dry by N₂ flow.

For film UV-Vis study, ultrathin P3HT film was also prepare on thin glass slide following the procedure of P3HT film on ITO mentioned above. The preparation of undoped, doped and partially dedoped samples on glass slides also followed the same procedure. The prepared glass slides were blown dry by N₂ flow.

Characterizations

UV-vis spectroscopy was performed on a Cary 60 UV-vis spectrometer. AFM and Kelvin Probe Force Microscopy (KPFM) measurements were carried out on a NTEGRA Prima AFM from NT-MDT. Topography measurements were taken under semi-contact mode using microfabricated Pt-coated silicon tips (µMasch NSC18-Pt) with a typical resonant frequency of 75 kHz and a spring force constant of 1.2–5.5 N/m. To partially expose the ITO substrate as an internal reference, same AFM tips were employed in lithography mode to impact the surface. KPFM images were recorded in two-pass mode using Pt-coated tips. The first pass of KPFM was performed in tapping mode, recording the topography. A second pass with a lift height of 10 nm followed the obtained topography. A bias was applied to the AFM tip during the second pass, $V_{tip} = V_{dc} + V_{ac} \sin(\omega_{act})$, where V_{dc} is the dc offset voltage and V_{ac} is the ac voltage applied at frequency of ω_{ac} . Typically ω_{ac} is selected at the tip resonant frequency in the

second pass to maximize the sensitivity. A lock-in amplifier is used to extract the electrostatic force modulated at frequency ω_{ac} , $F\omega_{ac} = (\partial C/\partial z)(V_{dc} - \Delta\phi)V_{ac} \sin(\omega t)$, where $\Delta\phi$ is the contact potential difference (CPD), or namely the work function difference between tip and sample due to the equilibrium of Fermi levels. $F\omega_{ac}$ is nullified when the feedback controller sets $V_{dc} = \Delta\phi$, which equals local CPD. Since in this work, ITO substrate was deliberately exposed, the difference in CPD value between film and ITO region can be directly interpreted as the difference in their work functions without concerning the work function variations of Pt-Coated silicon tip.

Device Fabrication and Charge Transport Measurements

Quartz substrates were cleaned using detergent in deionized water, acetone, then isopropyl alcohol for 15 min sequentially under sonication and dried in an oven. Gold electrodes (40 nm) were thermally evaporated at 1×10^{-7} torr using a shadow mask on top of the quartz. The defined channel was 30 μm long and 1 mm wide. 40 μL of 1 mg mL^{-1} P3HT stock solution in toluene was spin-coated at 2000 rpm for 120 s to give a ~ 2.5 nm thick film. Doped samples were made by applying a 225 $\mu\text{g mL}^{-1}$ F₄-TCNQ solution in acetonitrile on the P3HT-coated substrate for 60 s. After this time, the substrate was spun at 1500 rpm for 30 s, resulting in a ~ 3.5 nm thick film. Devices were tested on a Signatone 1160 series probe station inside a nitrogen glovebox. Data was collected by a Keithley 4200 semiconductor characterization system.

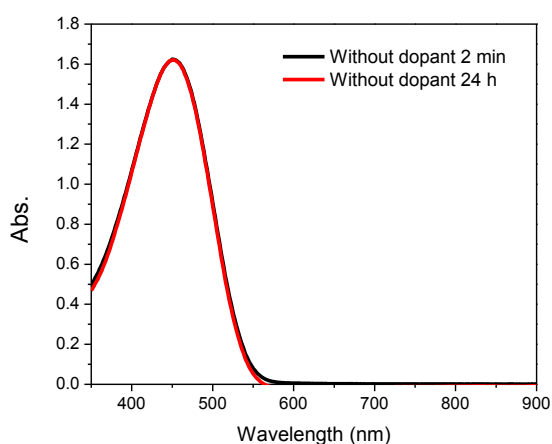


Figure S1. UV-Vis spectra of 167 $\mu\text{g/mL}$ LMW-P3HT in toluene. Single absorbance peaks at 450 nm attributed to the π - π^* transition peak of s-P3HT in solution are observed both in freshly made and aged samples, indicating LMW-P3HT in toluene remains in solubilized state without any aggregation.

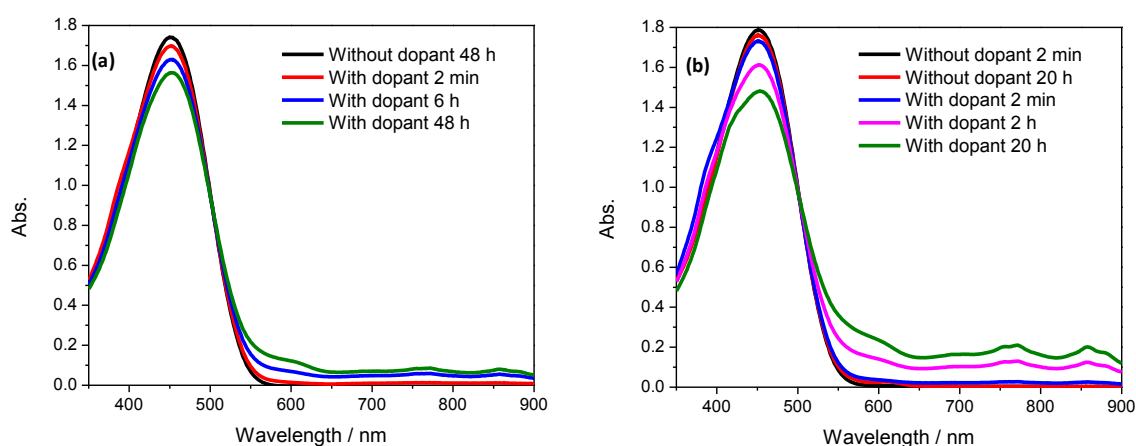


Figure S2. Evolution of UV-Vis spectra of 167 $\mu\text{g/mL}$ LMW P3HT in binary solvents, 25% decane in toluene (a) and 30% decane in toluene (b) before and after addition of 3.7 wt% F₄-TCNQ dopant. After the addition of dopant, the absorbance bands centered at 768 and 850 nm emerged gradually, which corresponded to the doping products of P3HT polaron/bipolaron and F₄-TCNQ anion. The doping reaction proceeds faster in 30% decane in toluene than in 25% decane in toluene.

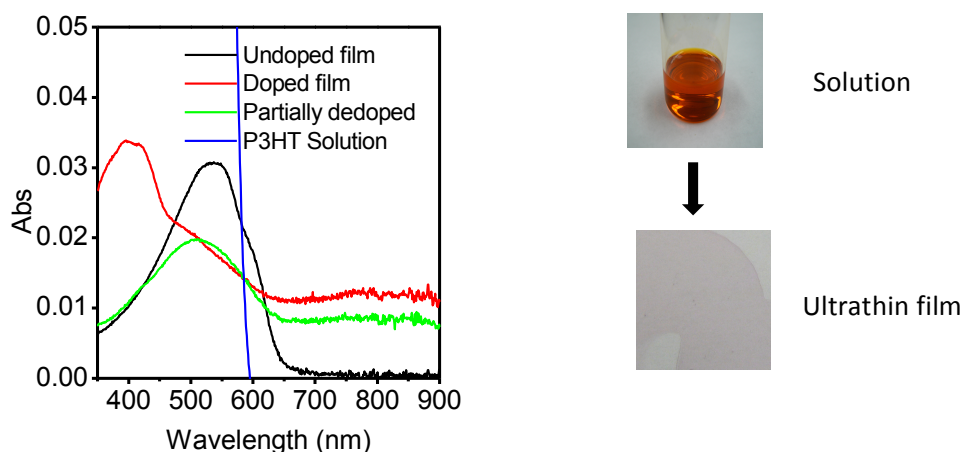


Figure S3. UV-Vis spectra of 1mg/mL LMW P3HT in toluene stock solution, ultrathin film prepared from spin-coating of the stock solution, the doped ultrathin film and the partially dedoped ultrathin film. No observable absorbance peaks at 615 nm and 565 nm associated with the vibronic 0–0 and 0–1 vibronic transitions can be observed, indicating 1 mg/mL P3HT toluene solution is free from forming π – π stacking aggregates. Peak at 450 nm of s-P3HT in solution is not shown here because its intensity is out of range of the instrument. The purple P3HT film prepared from drop-casting of the stock solution shows characteristic absorbance of P3HT aggregates at 565nm and 615nm. After “orthogonal doping” by F_4 -TCNQ solution, absorption bands of doping product emerge along with a drastic decrease of the vibronic 0–0 and 0–1 peaks. This indicates the transition of undoped aggregates into doped polarons.

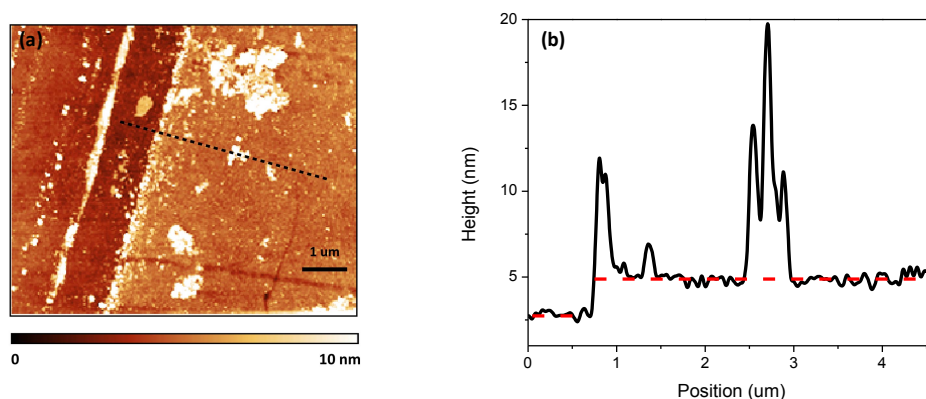


Figure S4. (a) AFM height image of an area of P3HT deposited ITO with a tweezer-made scratch. P3HT film is on the right and exposed ITO is on the left. (b) Height profile as marked in (a). The height difference between ITO and P3HT film is about 2.5 nm.

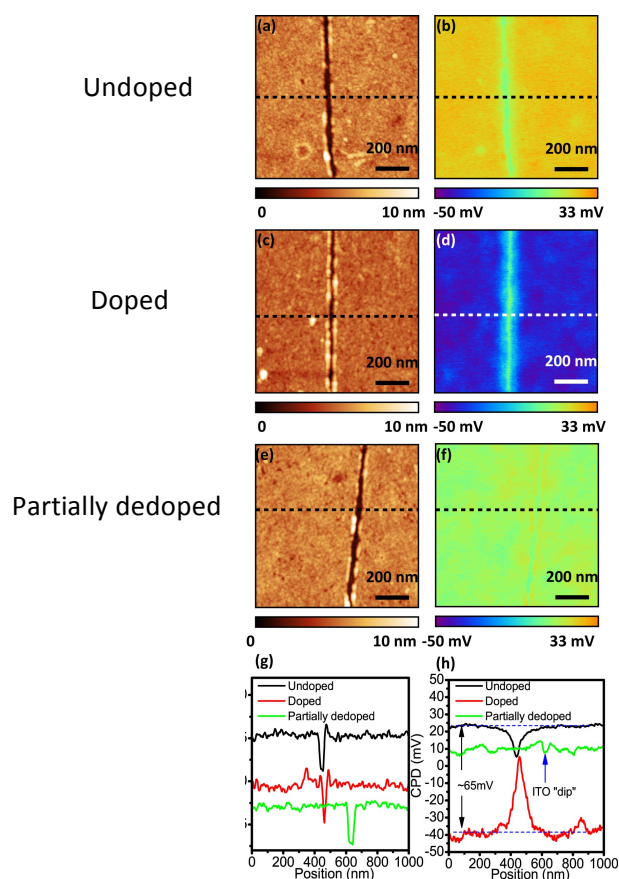


Figure S5. AFM and KPFM results on solid P3HT films prepared from spin-coating 1 mg/ml LMW P3HT in toluene on ITO substrate with and without subsequent doping in 225 $\mu\text{g/mL}$ $\text{F}_4\text{-TCNQ}$ acetonitrile solution. AFM morphology of pristine P3HT film (a), doped film (c) and partially dedoped film (e) resembles each other, showing features of a uniform film. Contact potential difference (CPD) of undoped film (b), doped film (d) show significant contrast referring to the exposed ITO substrate. However, “scratch” in the CPD of partially dedoped film (f) is almost indistinguishable. Panel (g) shows the CPD profiles of undoped, doped and partially dedoped P3HT film as marked in panel (b), (d) and (f). CPD of undoped P3HT film (h) is 65 mV higher than doped film and 15 mV higher than ITO. While partially dedoped film (h) has a similar CPD compared to ITO, which is in consist with the lower “visibility” of the scratch in Panel (f). Height profiles were vertically shifted for reading convenience while CPD profiles were not shifted. Arrow in Panel (h) marks the ITO “dip” in the CPD profile for partially dedoped film.

Table S1. Summary of film Thickness (d) and conductivity (σ) between undoped and doped samples.

	d (nm)	σ (S/cm)
Undoped film		
Device 1	2.65 ± 0.20	4.71×10^{-6}
Device 2		9.14×10^{-6}
Device 3		4.96×10^{-5} (excluded*)
Device 4		9.45×10^{-6}
		Average 7.7×10^{-6}
Doped film		
Device 1	3.73 ± 0.45	1.24×10^{-1}
Device 2		1.27×10^{-1}
Device 3		1.17×10^{-1}
		Average 1.2×10^{-1}

*This piece of σ data failed in Student's t -test with a two-sided 95% confidence level.