Electronic Supplementary Information

Infrared Spectroscopy Depth Profiling of Organic Thin Films

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The Atomic Force Microscopy (AFM) images of P3HT film under different etching conditions.

AFM results of P3HT show little changes of surface roughness during glow discharge plasma etching at low pressure. Other treatment may lead to the increase of surface roughness. The UV-vis of P3HT films in the Fig. S1e are corresponding to the Fig. S1a-d, which are investigated to study the P3HT properties with different treatments. After the UV ozone etching, the main peak of P3HT film is blue-shifted and totally becomes “dead” materials. The treatment upon high pressure argon plasma could elevate the baseline at long wavelength from 700 nm to 1000 nm, while keep a similar shape to the main peak, indicating an oxidation reaction occurred at the surface of film during high pressure etching. Thus, the film is damaged to some extent. As for low pressure argon etching, the main peak has the identical shape compared with pure P3HT and just decrease in the intensity, suggesting that the treatment for film at low pressure protects the bulk materials below the surface. These results correspond well with the infrared spectra in the Fig. S1b. UV-vis absorption spectroscopy was performed in transmission under ambient conditions using a PG2000 PRO scientific Grade spectrometer (ideaoptics) for blend films with or without etching prepared on cleaned glass. AFM (Bruker Innova) was done on the incrementally etched upon a trapping mode.

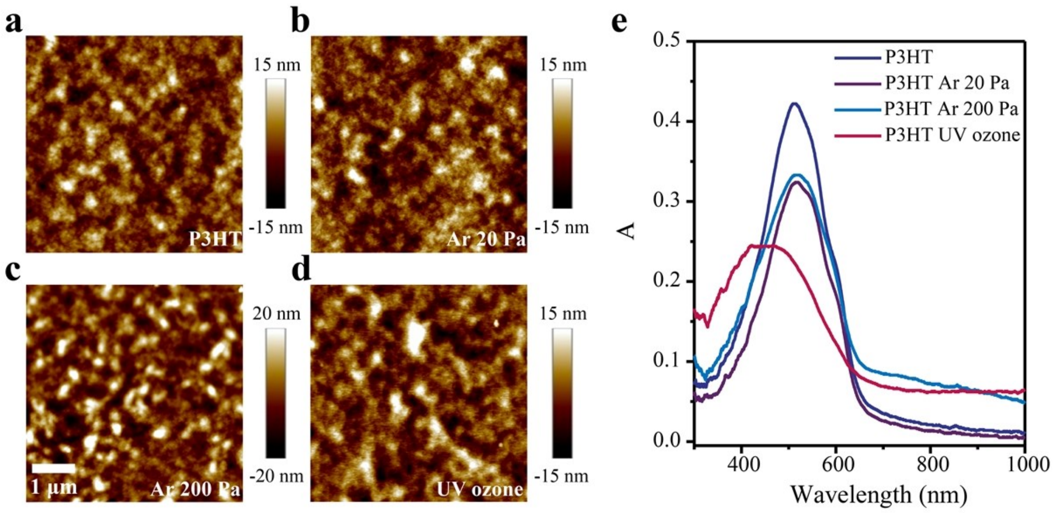

Fig. S1. a-d) AFM height images (5 μm × 5 μm) of P3HT films with different treatment conditions: untreated (a), treated by low pressure argon plasma (b), high pressure argon plasma (c) and UV ozone etching (d). The corresponding root-mean-square surface roughness values are 4.36, 4.97, 7.09 and 5.2 nm, respectively. e) The UV-vis absorption spectra of P3HT films were obtained from the films used in (a-d). The absorption plateau at wavelength 700 - 1000 nm is due to the damage (oxidation) of P3HT. Etching at low pressure (20 Pa) does not induce damage to the P3HT films below the etched surface. Therefore, low pressure “soft” glow plasma is the key to achieve FDD-IR spectroscopy.

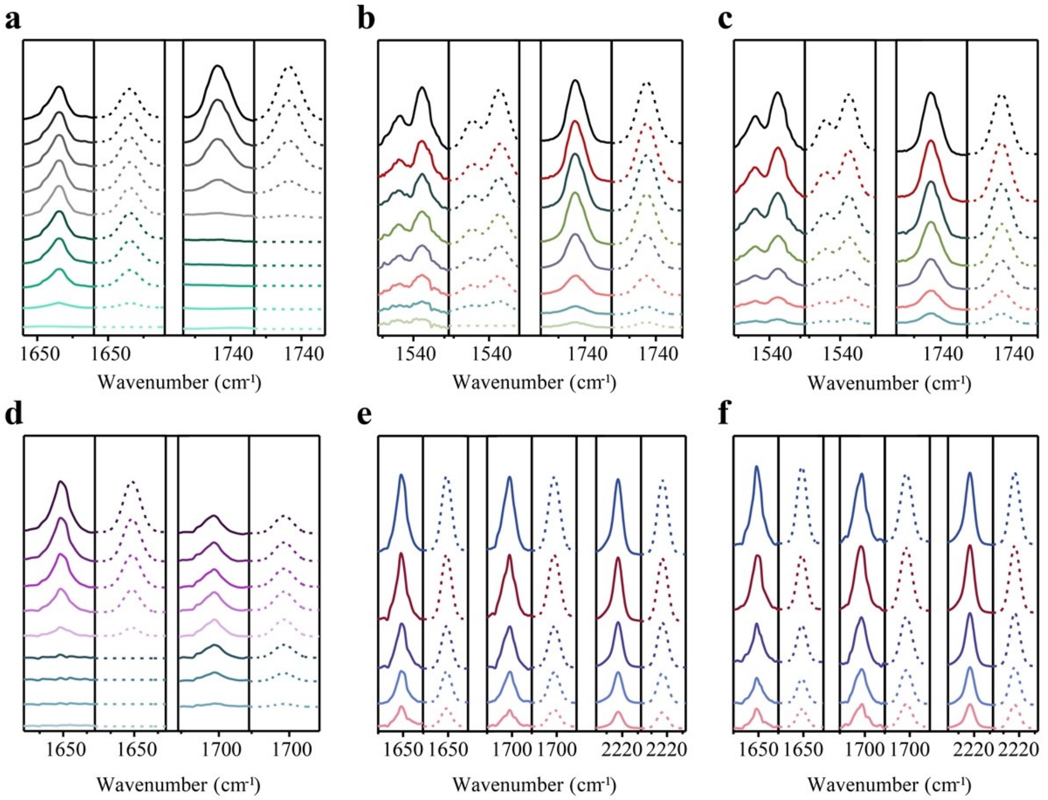

Fig. S2. The detailed Gaussian fitting process of infrared spectra: a) PMMA/PDPPDTT bilayer film, b) PMMA:PDPPDTT (4:1), c) PMMA:PDPPDTT (1:1) blend films, d) PM6/Y6 bilayer film, e) as-cast and f) solvent-annealed blend films. The solid lines are all from experimental measurements and derived from Fig. 3(a-c) and Fig. 4(a-c), while the dashed lines are Gaussian fitting results.

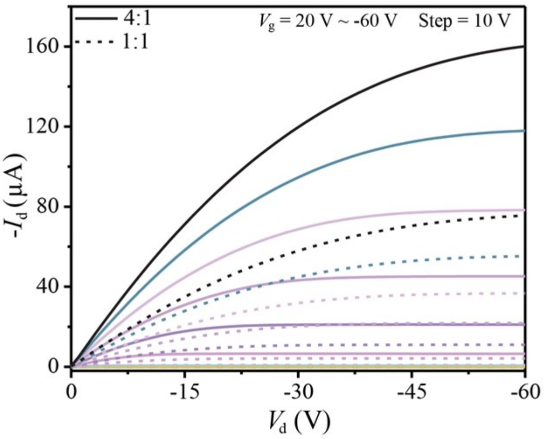

Fig. S3. Output curves of PMMA:PDPPDTT (4:1) and PMMA:PDPPDTT (1:1) OFETs.

The doping degree calculation of F4TCNQ/P3HT films.

It is necessary for us calculate initial doping degree for two kind of doped films. The peak at 2227 cm^{-1} (C≡N) is assigned to neutral F4TCNQ and is utilized to calculate doping degree. F4TCNQ was spin-coated on the cleaned CaF_2 (before doping) or on the pre-coated P3HT layer (after doping) under exactly the same conditions. The decrease of peak at 2227 cm^{-1} in absorbance can be attributed to reaction between dopant and host materials. For the F4TCNQ/P3HT films spin-coated from MeCN, the ratio of neutral F4TCNQ to charged F4TCNQ is 2.50:1. For the F4TCNQ/P3HT films spin-coated from co-solvent, the ratio of neutral F4TCNQ to charged F4TCNQ is 1.12:1.

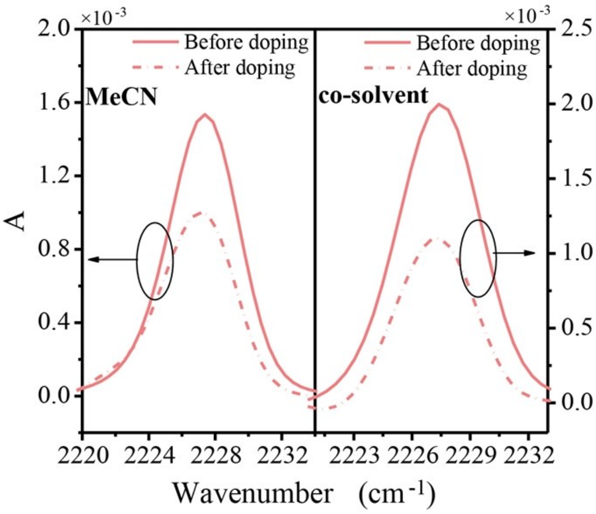

Fig. S4. The doping degree calculation of F4TCNQ/P3HT films fabricated upon sequentially processed method. F4TCNQ was spin-coated from MeCN (left) or co-solvent (right) onto pre-coated P3HT layer.

Charged cyano-group (C≡N) peak fitting for the dope organic semiconductors.

All resulting infrared spectra were baseline corrected and then subsequently fitted using OMNIC software. A Gaussian:Lorentzian shape was used to fit two kinds of F4TCNQ doped P3HT bilayer films. Clear asymmetry in the infrared spectra required one or two additional peaks for adequate fitting. Some peaks may have an error of ±1 cm^{-1} during the fitting process compared with peak position data given in the literature.

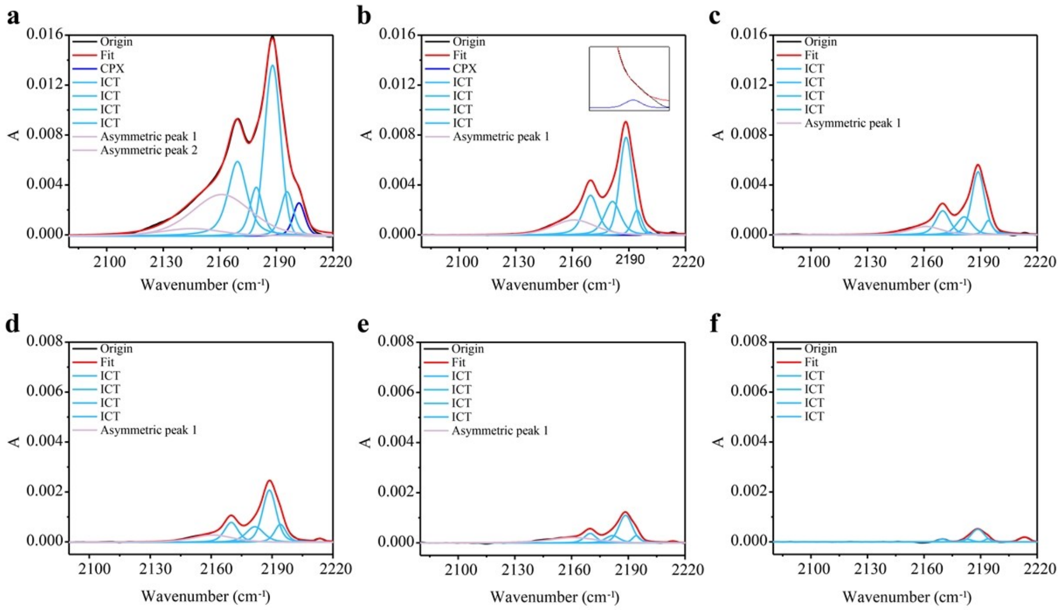

Fig. S5. a-f) The detailed Gaussian:Lorentzian fitting process of infrared spectra for F4TCNQ/P3HT films fabricated upon sequentially processed method. F4TCNQ was spin-coated from MeCN onto pre-coated P3HT layer. Red line is the sum of fitting results. Light blue lines correspond to spectral fits for ICT peaks. Dark blue lines correspond to spectral fits for CPX peaks. Light red lines are used to fit the clear asymmetry in the spectra. The inserted figure in the Fig. S5b is a magnification of CPX state.

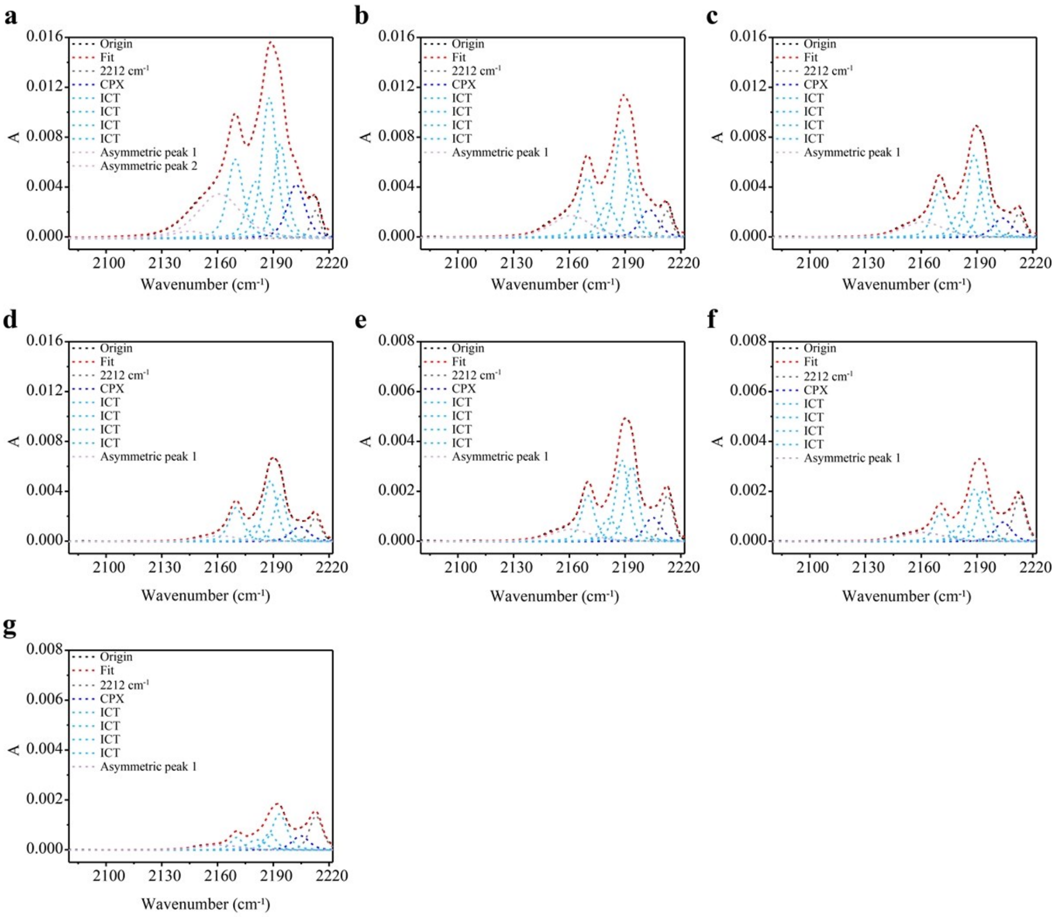

Fig. S6. a-g) The detailed Gaussian:Lorentzian fitting process of infrared spectra for F4TCNQ/P3HT films fabricated upon sequentially processed method. F4TCNQ was spin-coated from co-solvent onto pre-coated P3HT layer. Red dash line is the sum of fitting results. Light blue dash lines correspond to spectral fits for ICT peaks. Dark blue dash lines correspond to spectral fits for CPX peaks. Light red dash lines are used to fit the clear asymmetry in the spectra.

The AFM images of as-cast PM6:Y6 blend films at low pressure argon plasma etching.

The AFM images of as-cast PM6:Y6 blend films show the height images of the surface for the blend films etched with 0, 3, 6 and 9 min. The thickness of etched film is estimated from UV-vis absorption spectroscopy in Fig. S7e. The initial thickness of the as-cast blend film is set as 100 nm. Utilizing different absorbance values of the etched films, the thickness of etched films could be easily obtained.

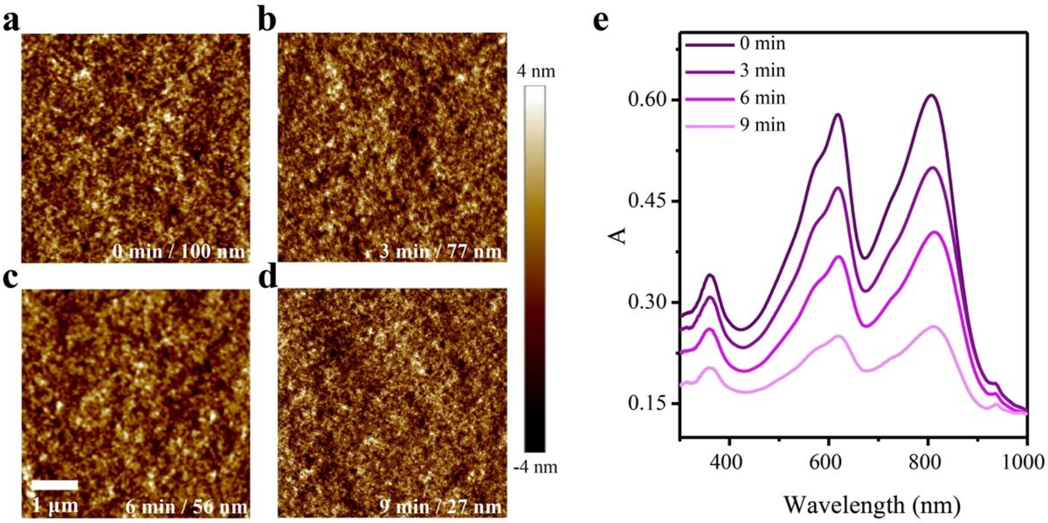

Fig. S7. a-d) AFM height images (5 μm × 5 μm) of PM6:Y6 blend films after etching for different time. The etching time and residual film thickness are provided in each micrograph. After etching for 0 min, 3 min, 6 min and 9 min, the root-mean-square (R_q) surface roughness values are 1.14, 1.17, 1.06 and 1.28 nm, indicting good miscibility between PM6 and Y6. e) The UV-vis absorption spectra of PM6:Y6 blend films after different etching time.

Table S1. Characteristic functional group peaks of some common organic electronic materials. The infrared absorption peaks were measured in this work.

Materials	The wavenumber of characteristic functional groups / cm^{-1}		Reference
	C=O	C≡N	
PBDB-T[a]	1646	-	-
PM6[a]	1647	-	-
PTB7-Th[a]	1704	-	-
ITIC[a]	1703	2217	-
ITTC[a]	1698	2215	-
ITCC[a]	1697	2219	-
ITIC-Th[a]	1704	2218	-
ITIC-Th1[a]	1702	2219	-
Y6[a]	1694	2213	-
IEICO[a]	1692	2215	-
IEICO-4F[a]	1691	2216	-
IT-4Cl[a]	1701	2220	-
$PC_{61}BM$[a]	1737	-	-
$PC_{71}BM$[a]	1732	-	-
PDPPDTT[a]	1661	-	-
PMMA[a]	1730	-	-
F4TCNQ[a]	-	2227	-
TCNQ[b]	-	2227	1
FTCNQ[b]	-	2224	1
F2TCNQ[b]	-	2231	1

[a] Dates from experimental measurements.

[b] Dates from literatures.

Reference

1 H. Mendez, G. Heimel, S. Winkler, J. Frisch, A. Opitz, K. Sauer, B. Wegner, M. Oehzelt, C. Rothel, S. Duhm, D. Tobbens, N. Koch, I. Salzmann, *Nat. Commun.* 2015, **6**, 8560.