Electronic Supplementary Information

Revealing Working Mechanisms of PFN as a Cathode Interlayer in Conventional and Inverted Polymer Solar Cells

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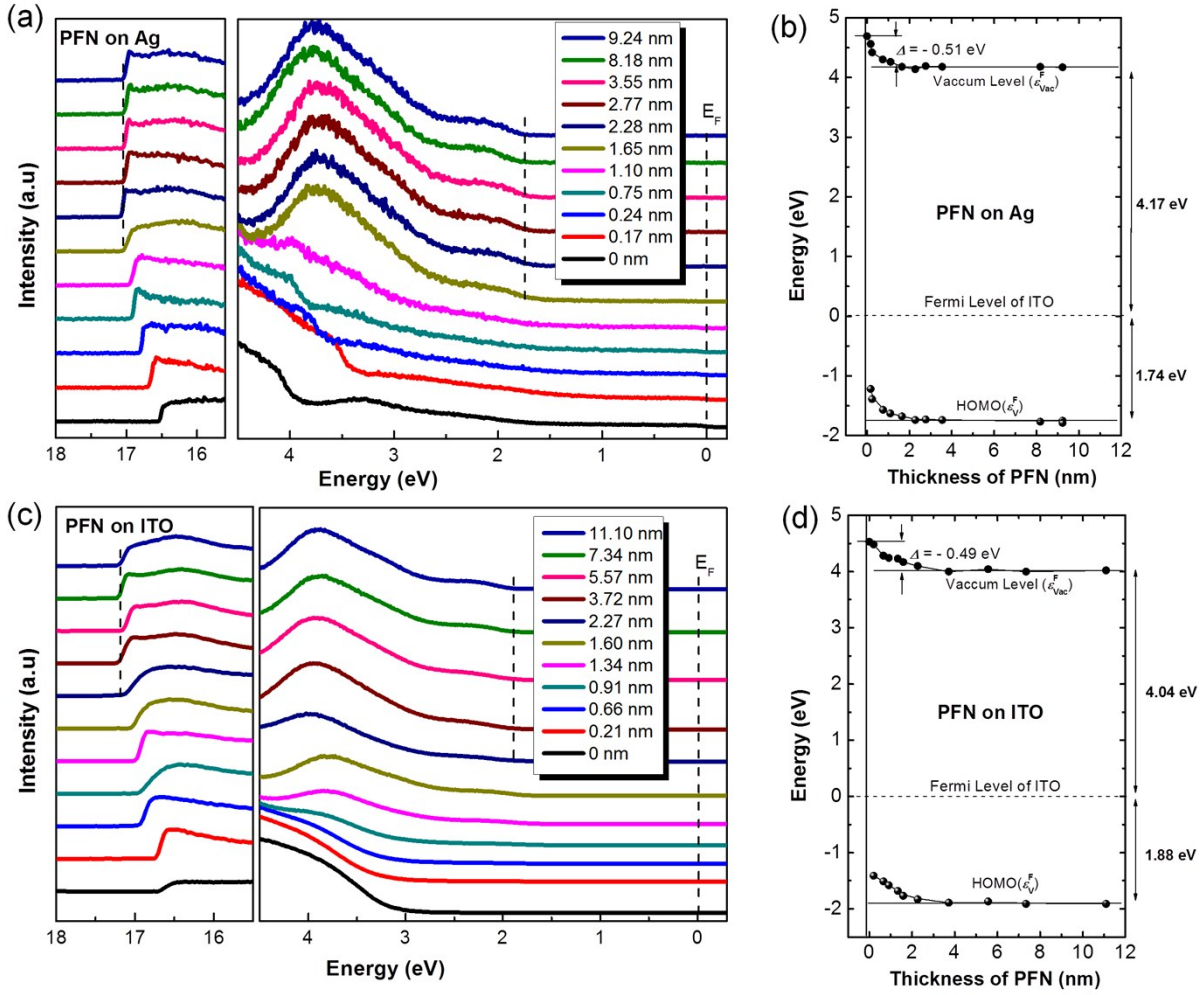

Figure S1. UPS spectra of various thickness PFN layer spin-coated on Ag (a) and ITO (c). Evolution of the WF and HOMO with the variation in thickness of PFN on Ag (b) and ITO (d).

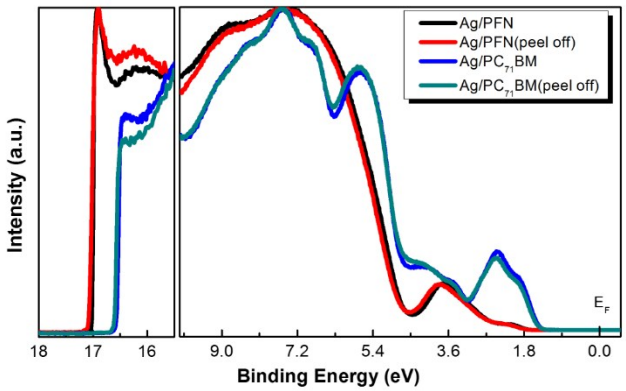

Figure S2. UPS spectra of PFN and $PC_{71}BM$ films prepared by spin-coating method and "Peel-off" method on Ag.

Table S1. Work function (ϕ), HOMO level *versus* Fermi level (E_{HOMO}) and HOMO level *versus* vacuum level (*IP*) of PFN and $PC_{71}BM$ films prepared by spin-coating method and "Peel-off" method on Ag. All values are shown in unit of eV.

Devices	Φ_{WF}	E_{HOMO}	*IP*
Ag/PFN	4.19	1.72	5.91
Ag/PFN(peel off)	4.16	1.76	5.92
Ag/$PC_{71}BM$	4.66	1.46	6.12
Ag/$PC_{71}BM$(peel off)	4.62	1.48	6.10

Table S2. Work function (ϕ), HOMO level *versus* Fermi level (E_{HOMO}) and HOMO level *versus* vacuum level (*IP*) of Al/LiF covered by various organic films.

Devices	ϕ	E_{HOMO}	IP
Al/LiF	3.45	-	-
Al/LiF/$PC_{71}BM$	4.32	1.81	6.13
Al/LiF/$PC_{71}BM$/PFN(0.07 nm)	4.22	1.80	6.05
Al/LiF/$PC_{71}BM$/PFN(0.25 nm)	4.13	1.82	5.95
Al/LiF/$PC_{71}BM$/PFN(0.44 nm)	4.09	1.84	5.93
Al/LiF/$PC_{71}BM$/PFN(0.65 nm)	4.06	1.83	5.91
Al/LiF/$PC_{71}BM$/PFN(1.04 nm)	4.01	1.90	5.91
Al/LiF/$PC_{71}BM$/PFN(3.08 nm)	3.91	1.98	5.89

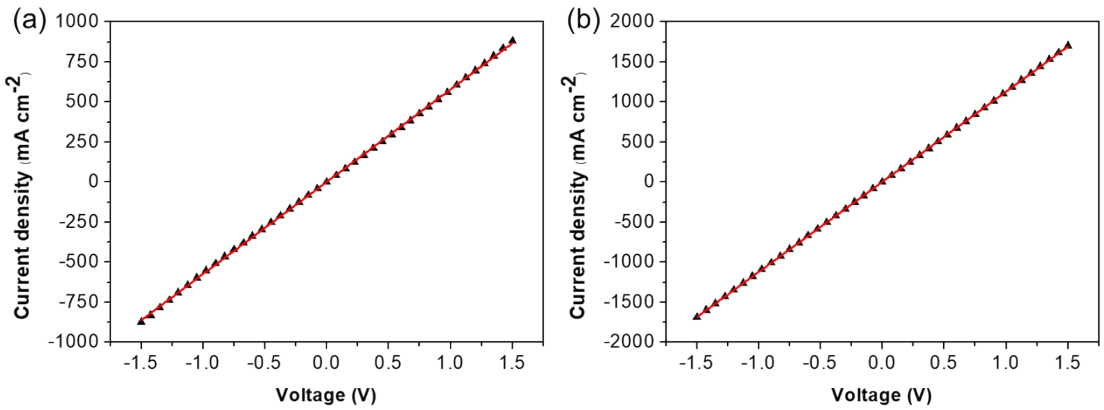

Figure S3. Conductivity measurements of $PC_{71}BM$ in (a) ITO/$PC_{71}BM$(20nm)/PFN(2nm)/Al and (b) ITO/PFN(2nm)/$PC_{71}BM$(20nm)/Al.

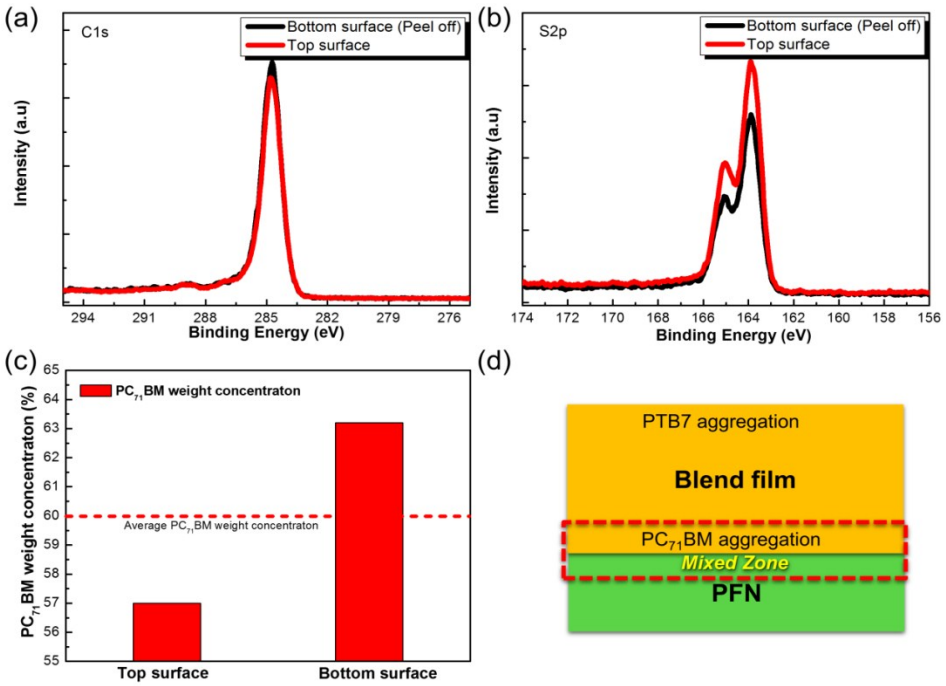

Figure S4. XPS spectra of (a) C1s and (b) S2p of PTB7:$PC_{71}BM$ blend film at top and bottom surfaces. (c) The $PC_{71}BM$ weight concentration in the blend film at top and bottom surfaces. (d) Schematic illustration for distribution of PTB7 and $PC_{71}BM$ in the blend film.