Supporting Information

Liquid-Crystalline Ionic Liquids Modified Conductive Polymers as Transparent Electrode for Indium-Free Polymer Solar Cells

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Characterization of PH1000 and PH1000/LCIL films: The thickness of PH1000 films and PH1000/LCIL films were measured by Ambios Technology Ltd. XP-2 surface profilometer. Transmission spectra of films were measured by UV-Vis spectroscopy (Perkin-Elmer Lambda 750). Morphologies of all films were investigated by scanning electron microscopy (SEM, Hitachi SU8020) and AFM (Digital Instrumental Nanoscope 31) in the tapping mode. The transmission electron microscopy (TEM; JEOL, JEM-2100F, field emission transmission electron microscope). PH1000 and ILCs modified PH1000 samples for TEM analysis were prepared through drop 15 μL PH1000 (dilution by deionized water (1:4 by volume)) on the copper TEM grid and then annealed in ambient atmosphere at 120 ^{o}C for 20 min. By drop 10 μL LCIL DMF solution (1.75mg mL^{-1}) on the dried PH1000 films to afford the PH1000/LCIL films, then annealed in ambient atmosphere at 120 ^{o}C for 25 min. P3HT:PCBM samples for TEM analysis were prepared through spin-casting of the P3HT:PCBM solution (dilution by dichlorobenzene (1:4 by volume)) onto the PH1000 film or PH1000/LCIL films. The P3HT:PCBM films were floated onto deionized water and placed on a copper TEM grid, then annealed in ambient atmosphere at 150 ^{o}C for 10 min. X-Ray photoelectron spectroscopy (XPS) were performed on a Thermo-VG Scientific ESCALAB 250 photoelectron spectrometer using a monochromated Al Ka (1,486.6 eV) X-ray source. Sample etching was performed using Ar^{+} ions with a 3000

V accelerated voltage. The raster area was approximately 3.14 mm^2. Ultraviolet photo-electron spectroscopy (UPS) were measured by a AXIS-ULTRA DLD spectrometer (Kratos Analytical Ltd.) with a He (I) (21.21 eV) monochromatic light source. Water contact angle measurements for films were characterized on JC2000A contact angle instrument. The work function measurement of the films were done by Kelvin probe (RHC020, KP Technology Ltd.). Sheet resistances of PEDOT:PSS films and PEDOT:PSS/LCIL films were measured by a four point probe. The wide-angle X-ray diffraction (WAXD) analysis was carried out on a Bruker D8 Focus X-ray diffractometer, operating at 40 kV and 40 mA with a copper target (k=1.54 A ˚). The scanning 2 hangle ranged between 2^o and 30^o with a step-scanning rate of 2^o/min. The PH1000 and PH1000/LCIL films were prepared by drop-casting 300 μL filtered PH1000 solution onto glass substrates and annealed on a hot plate in ambient atmosphere at 120 ^{o}C for 25 min. by following the same process as previous described. Texture observations by polarizing optical microscopy (POM) were made with a Nikon E600POL polarizing optical microscope equipped.

Characterization of PSCs: The current-voltage (*J-V*) measurements are characterized using a keithley 2400 source meter unit. The photocurrents are measured under an AM 1.5 G illumination at 100 mW cm^{-2}, using an Oriel 96000 150W solar simulator source. Incident photon-to-current efficiency (IPCE) was measured under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon cell. The light intensity is determined by using a silicon detector (with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL, Golden, CO).

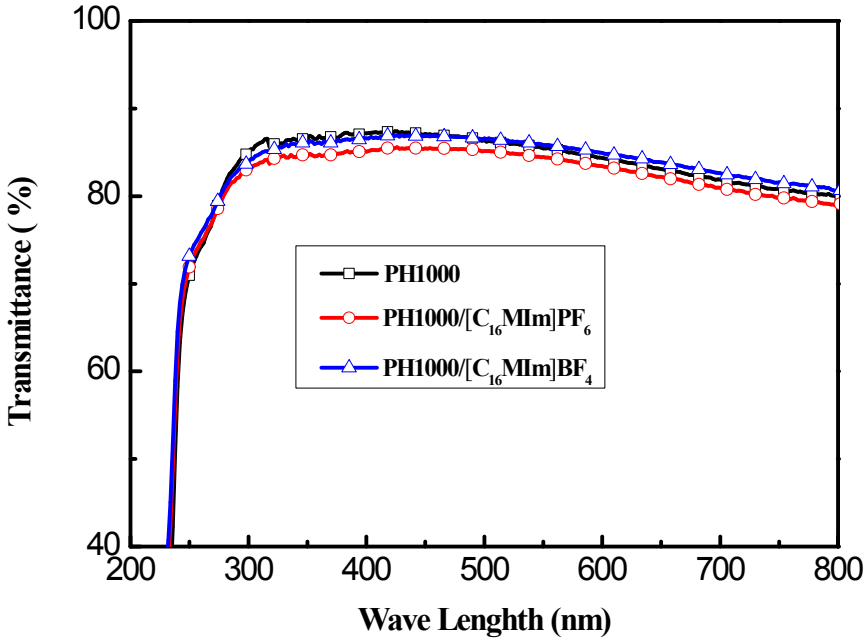

Figure S1. Transmittance of PH1000 film and Liquid-crystalline ionic liquids modified PH1000 films.

The work function measurement of PH1000 and ILCs modified PH1000 films were done using Kelvin probe. The samples were measured in a controlled chamber where the O_2 level is < 25 ppm. The work function discussed here is the average value of 144 points. The total 144 points are measured over the scan area 1.2 mm×1.2 mm. The surface potentials shown in **Figure S2** are values respect to the probe tip (5.10 eV). Therefore, the actual work functions of the electrodes were obtained by offsetting the work function of probe tip.

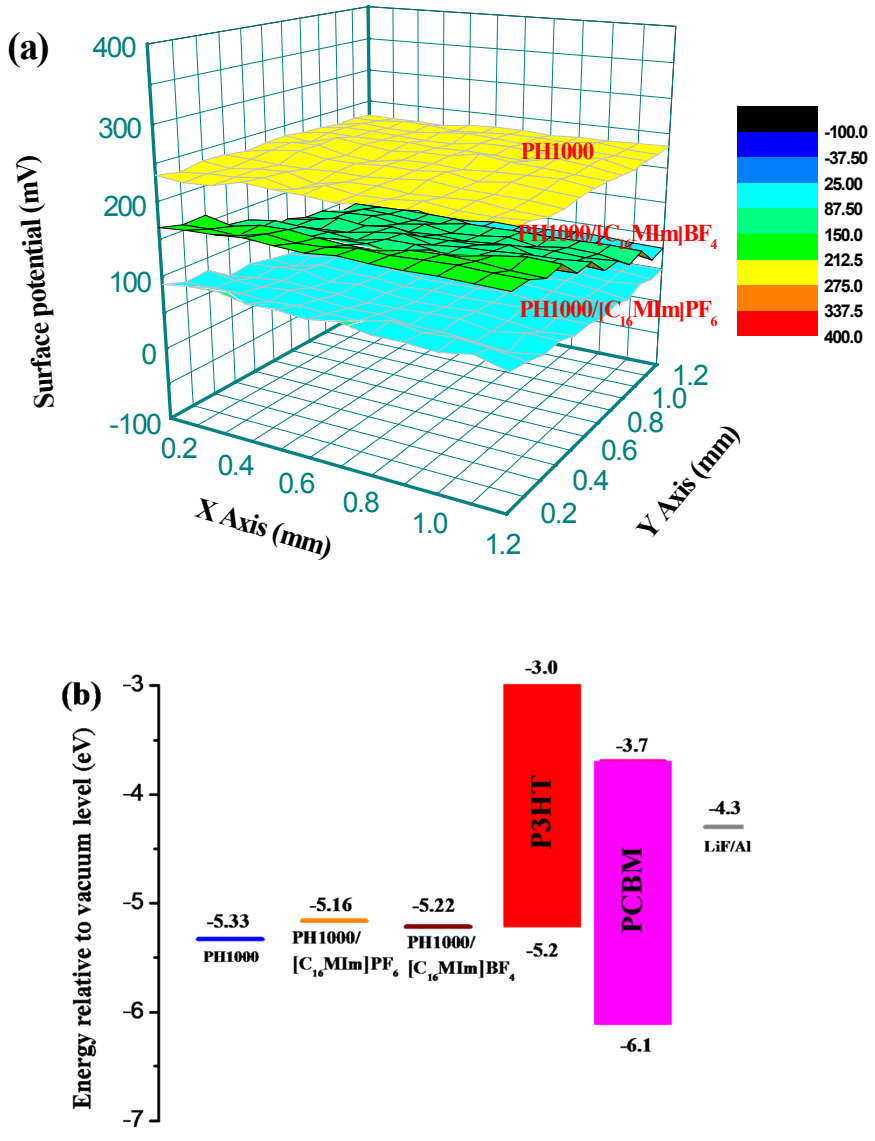

Figure S2 (a) Work function of PH1000 film and Liquid-crystalline ionic liquids modified PH1000 films. (b) Energy band diagram of the devices.

Table S1 Work function of pristine PH1000 and $[C_{16}MIm]PF_6$ or $[C_{16}MIm]BF_4$ modified PH1000 films measured using UPS and Kelvin Probe.

	Work function (Kelvin Probe) (eV)	Work function (UPS) (eV)
PH1000	5.33	5.15
PH1000/$[C_{16}MIm]PF_6$	5.16	4.94
PH1000/$[C_{16}MIm]BF_4$	5.22	5.01

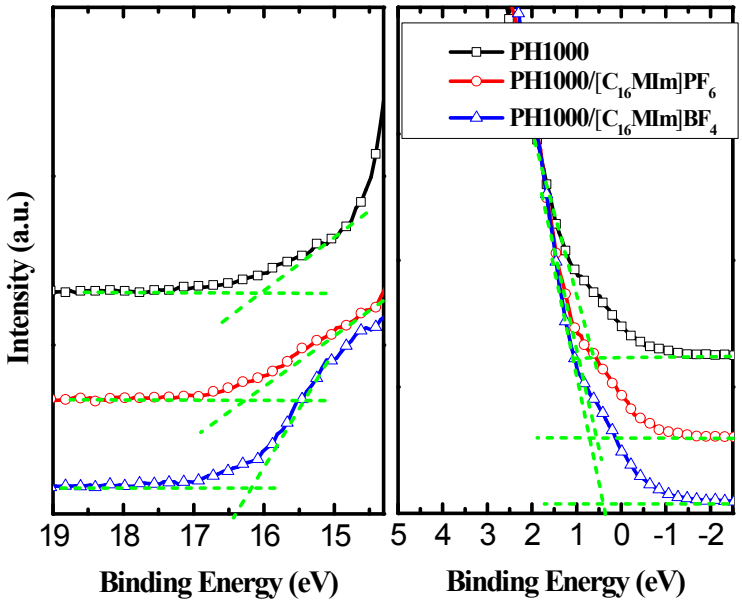

Figure S3 UPS spectra of PH1000 and $[C_{16}MIm]PF_6$ or $[C_{16}MIm]BF_4$ modified PH1000 films.

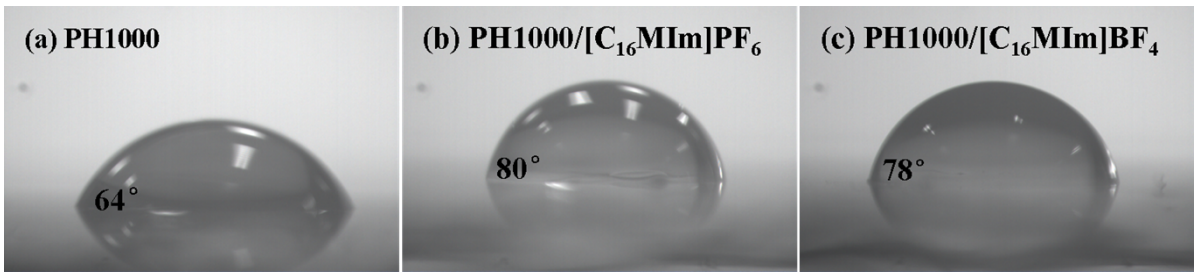

Figure S4 The contact angle measurements of (a) PH1000, (b) PH1000/$[C_{16}MIm]PF_6$, (c) PH1000/$[C_{16}MIm]BF_4$ films.

Table S2 show the electrical property of pristine PH1000 film and modified PH1000 films. In this test, the PH1000 with a nominal thickness about of 80nm, and the PH1000/$[C_{16}MIm]PF_6$ films with a thickness about of 70 nm, the PH1000/$[C_{16}MIm]BF_4$ films with a thickness about of 60 nm.

Table S2 Electrical properties of P1000 film, $[C_{16}MIm]PF_6$ or $[C_{16}MIm]BF_4$ modified PH1000 films.

Electrode	Sheet resistance (Ω sq^{-1})	Conductivities ($S.cm^{-1}$)
PH1000	3.15×10^5	0.40
PH1000/$[C_{16}MIm]PF_6$	98	1457.7
PH1000/$[C_{16}MIm]BF_4$	134	1243.8

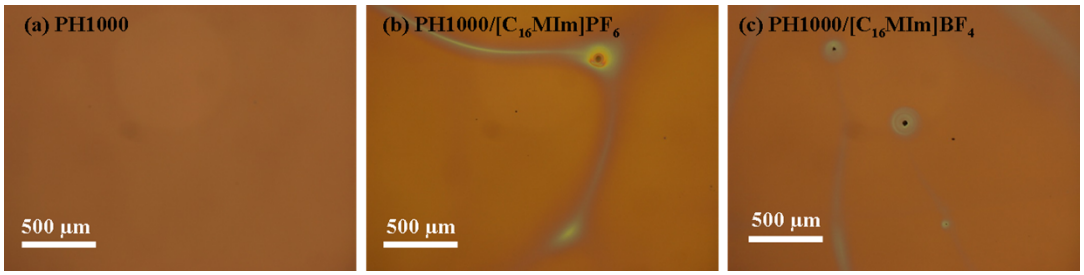

Figure S5. Polarized optical micrographs of (a) PH1000 film, (b) PH1000/$[C_{16}MIm]PF_6$ film and (c) PH1000/$[C_{16}MIm]BF_4$ film.

Table S3 The F atom content of the PH1000, PH1000/$[C_{16}MIm]PF_6$, PH1000/$[C_{16}MIm]BF_4$ films, and those films after etching for 60 s and 120 s.

	without etching (F At %)	etching for 60 s (F At %)	etching for 120 s (F At %)
PH1000	0.06	0	0
PH1000/$[C_{16}MIm]PF_6$	0.65	0.34	0.31
PH1000/$[C_{16}MIm]BF_4$	0.12	0	0

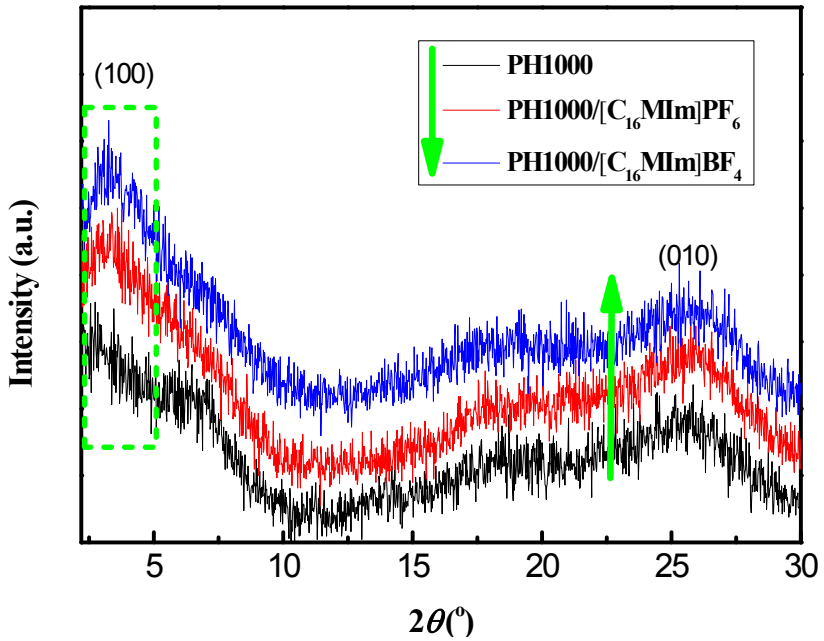

Figure S6 X-ray diffractograms measured from the pristine PH1000 film and $[C_{16}MIm]PF_6$ or $[C_{16}MIm]BF_4$ modified PH1000 films.

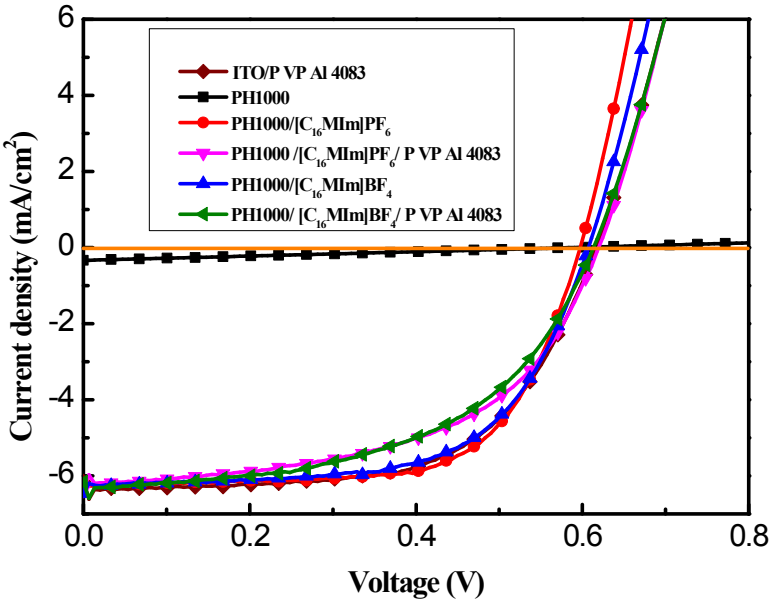

Figure S7 J-V curves of P3HT:$PC_{61}BM$ BHJ-PSC devices with an effective area of 18 mm^2, using ITO, PH1000, PH1000/$[C_{16}MIm]PF_6$ and PH1000/$[C_{16}MIm]BF_4$ films as the transparent anodes. The measurements were carried out under AM 1.5G illumination at an irradiation intensity of 100 mW cm^{-2}.

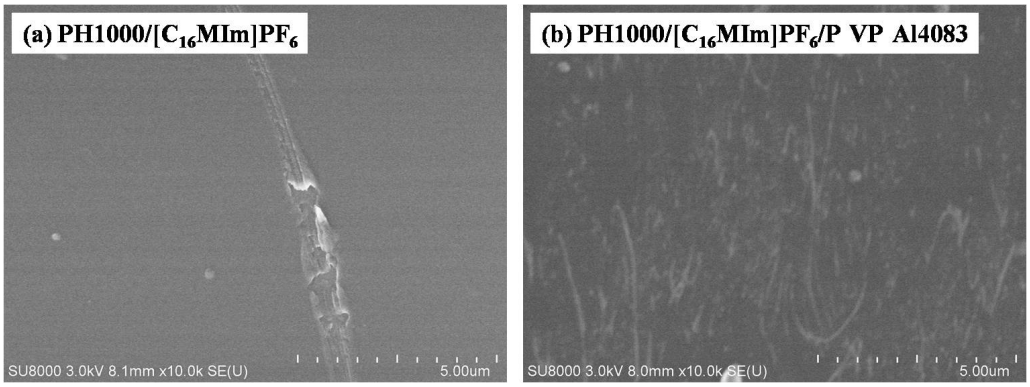

Figure S8 SEM images of (a) PH1000/$[C_{16}MIm]PF_6$ film, (b). PH1000/$[C_{16}MIm]PF_6$/P VP Al 4083 film.

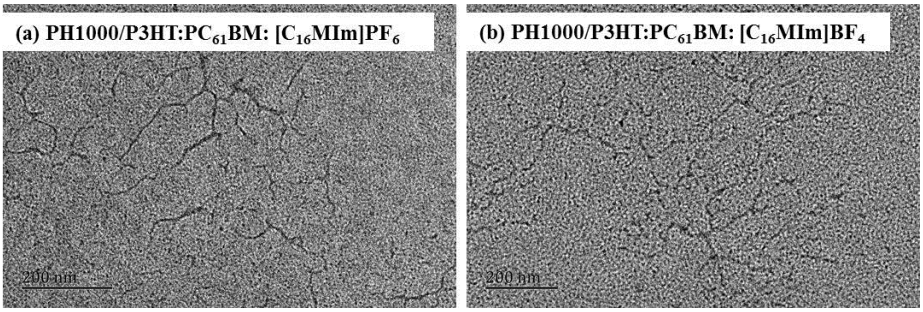

Figure S9 TEM images of P3HT:$PC_{61}BM$ blend with (a) $[C_{16}MIm]PF_6$ film and (b) $[C_{16}MIm]BF_4$ film on top of the pristine PH1000 films.

References

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