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Electronic Supplementary Information

Polymeric Ionic Liquid as Cathode Interlayer of Organic Photovoltaics with Improved Reproducibility

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Experimental Section

Materials and methods: The PTB7-Th and the (6,6)-Phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) were purchased from Solarmer Materials Inc. Other materials were purchased from Adamas, Aldrich, and Alfa and used without any further purification. ^1H NMR (400 MHz) spectra were measured on a Bruker 400 MHz AVANCE III with tetramethylsilane as an internal reference. The molecular weight was measured by the GPC on the Waters 1525 (Agilent PLgel 5 μm MIXED-C column) with polystyrene as the standard and DMF as the eluent. Tapping-mode AFM images thinness of film and work function data were obtained by using a scanning probe microscope and scanning Kelvin probe microscopy (SKPM) on a Bruker Metrology Nanoscope III-D. Electrochemical impedance spectroscopy (EIS) was measured by using an electrochemical workstation (CHI600D) with a frequency range from 1 Hz to 10 MHz in dark environment. SEM images were taken by a Quanta 200F microscope (FEI

Company) with an accelerating voltage of 20 kV. The thermal property of the polymer was characterized on SETSYS 16/18, SETARAM, France. The molecular weight was measured by the GPC on the Waters 1525 (Agilent PLgel 5 μm MIXED-C column) with the polystyrene as the standard and the DMF as the eluent.

Device fabrication and characterization: Photovoltaic devices were fabricated with a structure of glass/ITO/PEDOT:PSS/PTB7-Th:$PC_{71}BM$/CIL/Al. The ITO-coated glass substrates were cleaned by deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each and followed by a UV ozone treatment for 10 min. Then, PEDOT:PSS layer was spin-coated on the cleaned ITO surface. After being baked at 150 °C for 20 min, the active layer was spin-coated from a PTB7-Th/$PC_{71}BM$ (12 mg/mL, 1:1.5, w/w) in CB solution with 3% DIO at 1500 rpm for 1 min. The CIL was spin-coated in methanol solution at 4000 rpm for 30 s. Finally, a 75 nm Al layer were deposited on the active layer. The *J-V* measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100 mV cm^{-2}. The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (QE-R, Enlitech).

Synthesis of the polymeric ionic liquid (PIL): 1-Vinyl-3-butylimidazolium bromide (MIL, 1.190 g, 5.148 mmol) and AIBN (0.015 g, 0.091 mmol) as the initiator were placed into a 100 mL round-bottom flask then 20 mL chloroform was added. The polymerization was kept at 70 ^{o}C for 3.5 h in argon atmosphere. The polymer was precipitated in hexane and washed with hexane for three times. The product was

obtained as white solid by drying under vacuum in 70 °C for 12 h (0.923 g, 77.5%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.43-9.20 (m, 1H), 8.89-7.82 (m, 1H), 7.27-6.77 (m, 1H), 5.51-4.49 (m, 1H), 4.41-4.13 (m, 2H), 2.65-2.25 (m, 2H), 2.06-1.83 (m, 2H), 1.52-1.36 (m, 2H), 0.994-0.875 (m, 3H). Mn=34.8 kg/mol, PDI=1.91.

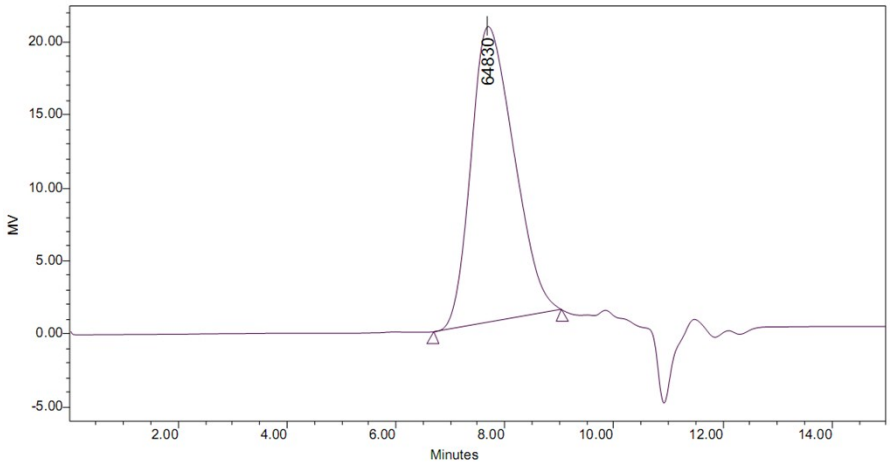

Figure S1. GPC curve of the PIL.

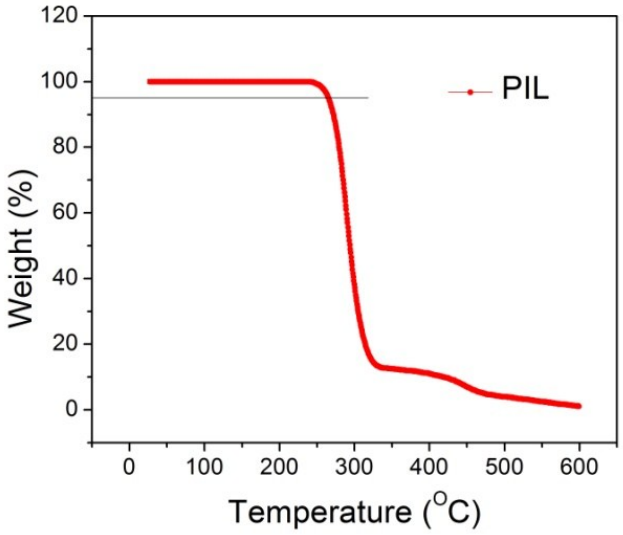

Figure S2. TGA curve of the PIL (heating rate: 10 °C min^{-1} in nitrogen atmosphere).

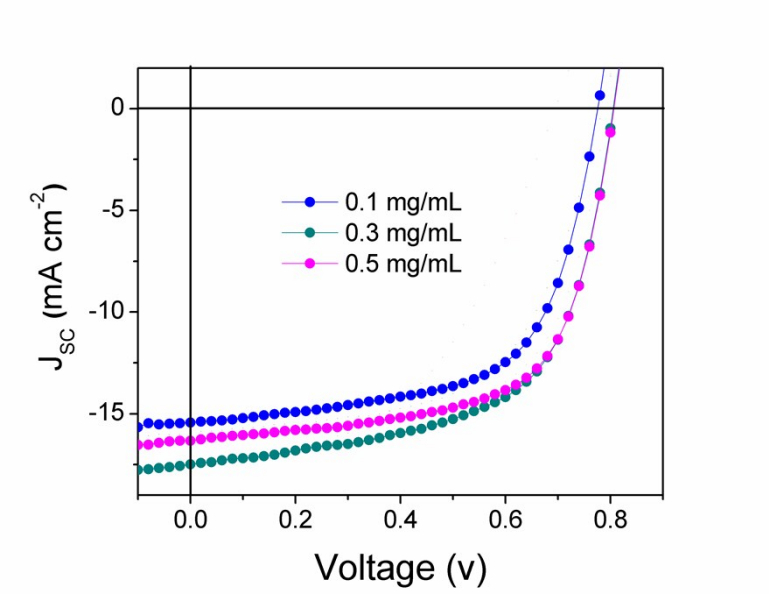

Figure S3. *J-V* curves of PIL-based devices with different concentrations of PIL in methanol.

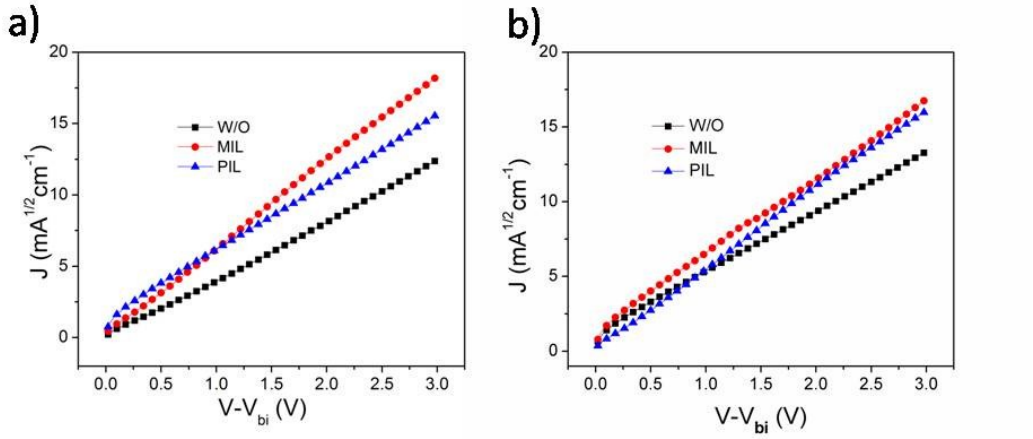

Figure S4. $J^{1/2}$-V fitting results of a) electron-only and b) hole-only devices for the mobility measurement using the SCLC model. The electron-only device structure for the mobility measurement is ITO/ZnO/PTB7-Th:PC71BM/MIL or PIL/Al. The hole-only device structure for the mobility measurement is ITO/PEDOT:PSS/PTB7-Th:PC71BM/MIL or PIL/Ag.

Table S1. Performances of devices based on the PIL spin-coated from different concentrations of PIL in methanol.

PIL in methanol	Thickness	J_{SC} (mA/cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
0.1 mg/mL	---	16.37	0.781	61.2	8.11 (8.02)[a]
0.3 mg/mL	2-3 nm	17.12	0.802	65.3	9.04 (8.66)
0.5 mg/mL	~5 nm	15.94	0.797	64.7	8.59 (8.37)

[a] Average PCEs obtained from 20 cells are shown in parentheses.

Table S2. Mobilities of the electron-only and hole-only devices with MIL and PIL as the interlayer, respectively.

Interlayer	μ_e (cm^2 V^{-1} S^{-1})	μ_h (cm^2 V^{-1} S^{-1})	μ_e/μ_h
MIL	1.15×10^{-3}	6.92×10^{-4}	1.66
PIL	8.03×10^{-4}	6.69×10^{-4}	1.20

[a] Electron-only device structure for the mobility measurement: ITO/ZnO/PTB7-Th:$PC_{71}BM$/MIL or PIL/Al.

[b] Hole-only device structure for the mobility measurement: ITO/PEDOT:PSS/PTB7-Th:$PC_{71}BM$/MIL or PIL/Ag.