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Supporting Information

Nonhalogen solvent-processed high efficiency polymer solar cells based on polymer donor containing chlorine and trialkylsilyl substituted thienyl benzodithiophene donor unit

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Experimental Section

Measurements: ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ on Bruker AV 400 MHz FT-NMR spectrometer. Elemental analysis was carried out on a flash EA1112 analyzer. Gel Permeation Chromatography (GPC) was carried out on Agilent Technologies PL-GPC-220 at 160 °C, where 1,2,4-tricholorobenzene as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) was measured on a Perkin-Elmer TGA-7 at a heating rate of 10 °C/min under inert atmosphere. UV-vis absorption spectrum was recorded on a UV-Vis-NIR Spectrophotometer of Agilent Technologies Cary Series, in which the extinction coefficient was defined by the absorption intensity of the active layer with a thick of 1 cm (*ca.* 60~80 nm for PBZ, PBZ-Cl and PBZ-ClSi). The electrochemical cyclic voltammetry (CV) was taken on a Electrochemical Workstation of Zahner Ennium IM6 in a acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), where glassy carbon disk, Ag/Ag^+ electrode, and Pt wire as working electrode, reference electrode and counter electrode, respectively. Photoluminescence (PL) spectra were taken on an Edinburgh Instrument FLS 980. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage. TEM was performed using a Tecnai G2 F20 S-TWIN instrument at 200 kV accelerating voltage, in which the blend films were prepared using a processing technique, as following: first, the blend films were spin-cast on the PEDOT:PSS/ITO substrates; second, the resulting blend film/PEDOT:PSS/ITO substrates were submerged in deionized water to make these blend films float onto the air-water interface; finally, the floated blend films were taken up on unsupported 200 mesh copper grids for a TEM measurement. Grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS) with a resonant photon energy of 284.8 eV.[1] Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11°-0.15°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. The crystal coherence length (CCL) was defined as CCL = 0.9 × (2π/FWHM) (Å), where FWHM is the full width at half maximum of the corresponding diffraction peak. Resonant soft X-ray scattering (RSoXS) transmission measurements were performed at beamline 11.0.1.2 at the ALS. Samples for RSoXS measurements were prepared on a PSS modified Si substrate under the same conditions as those used for device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100 nm thick Si3N4 membrane supported by a 5 mm × 5 mm, 200 μm thick Si frame (Norcada Inc.). 2-D scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The sample detector distance was calibrated from diffraction peaks of a triblock copolymer poly(isoprene-b-styrene-b-2-vinyl pyridine), which has a known spacing of 391 Å. The beam size at the sample is approximately 100 μm by 200 μm.

Fabrication and characterization of polymer solar cells. Polymer solar cell devices with a inverted device structure of ITO/ZnO/PFN/active layer/MoO_3/Al were fabricated under conditions as follows: patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 10-15 ohm/square was cleaned by a surfactant scrub and then underwent a wet-cleaning process inside an ultrasonic bath, beginning with deionized water followed by acetone and isopropanol. After oxygen plasma cleaning for 10 min, then the ZnO layer with a thickness of 30 nm was deposited by spin-coating under 2000 rpm for 60 s on top of the ITO substrate. ZnO nanoparticles were synthesized followed the literature.[2] The poly[(9,9-bis(3'-(*N*,*N*-dimethyl)-ethylammoinium-propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) was then deposited on top of the ZnO layer by spin-coating an methanol solution with a concentration of 0.2 mg/mL under 2000 rpm for 60 s. The active layer was then deposited on top of the PFN layer by spin-coating a blend solution of toluene and 1-phenylnaphthalene (PN) (20 or 40 mg mL^{-1}, dissolved 12 h under 100 ^{o}C) of polymer:IT-4F. The thickness of the active layer is measured on a KLA Tencor D-100 profilometer. Finally, 10 nm MoO_3 and 80 nm Al were successively deposited on the photosensitive layer under vacuum at a pressure of ca. 4×10^{-4} Pa, and through a shadow mask to determine the active area of the devices (0.2 cm^2). The PCE values of the PSCs were measured under a illumination of AM 1.5G (100 mW/cm^2) using a SS-F5-3A solar simulator (AAA grade, 50×50 mm^2 photobeam size) of Enli Technology CO., Ltd.. A 2×2 cm^2 monocrystalline silicon reference cell (SRC-00019) was purchased from Enli Technology CO., Ltd. PCE statistics were obtained using 20 or 10 individual devices fabricated under the same conditions. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 of Enli Technology CO., Ltd. The light intensity at each wavelength was calibrated with a standard single crystal Si photovoltaic cell. To study the charge generation and dissociation processes of the polymer:IT-4F-based PSCs, plots of the photocurrent (J_{ph}) *versus* effective voltage (V_{eff}) of the PSCs were measured. Here, J_{ph} and V_{eff} are defined as $J_{ph} = J_L - J_D$ and $V_{eff} = V_0 - V_{appl}$, respectively, where J_D and J_L are the photocurrent densities in the dark and under the illumination, and V_{appl} is the applied bias voltage and V_0 is the voltage at which $J_{ph} = 0$, respectively.[3] The J_{ph} reaches the saturation current density (J_{sat}) at high V_{eff} ($\geqslant$ 2 V in this case).

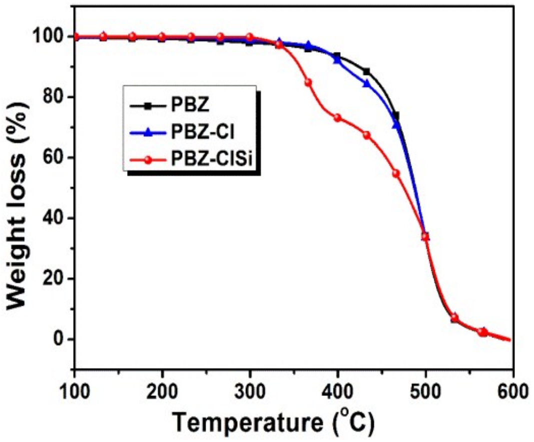

Fig. S1. The thermo-gravimetric analysis (TGA) plots of the polymer donors at a scan rate of 10 °C/min under nitrogen atmosphere.

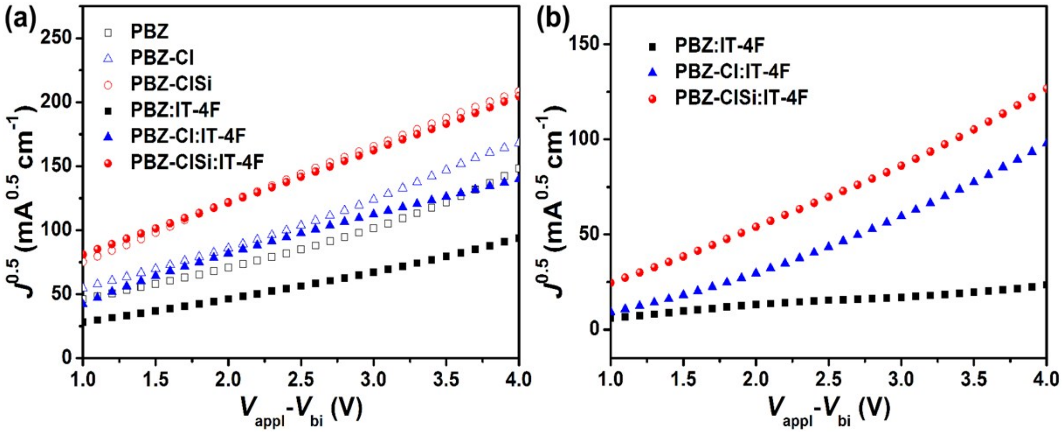

Fig. S2. The *J-V* curves of (a) the hole-only devices with the structure of ITO/PEDOT:PSS/polymers or polymers:IT-4F/MoO_3/Al; and (b) the electron-only devices with the structure of ITO/ZnO/polymers:IT-4F/Ca/Al according to the SCLC model.

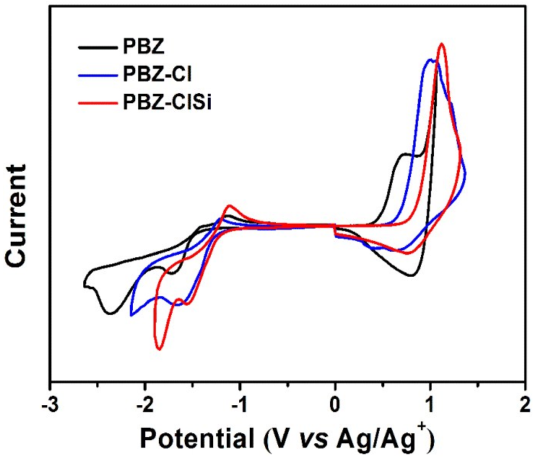

Fig. S3. Cyclic voltammogram of polymer films on a glassy carbon electrode measured in a 0.1 mol L^{-1} Bu_4NPF_6 acetonitrile solution at a scan rate of 50 mV s^{-1}.

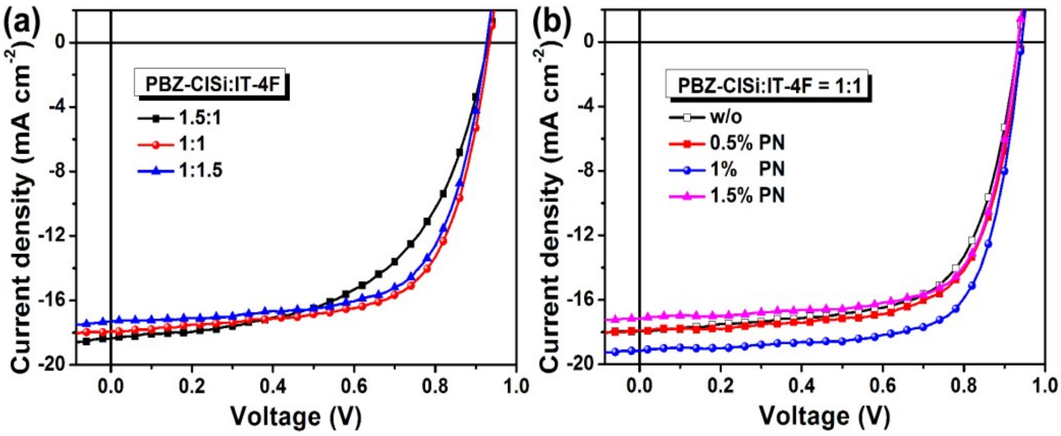

Fig. S4. The *J-V* plots of the PBZ-ClSi:IT-4F-based PSCs with (a) different D/A ratios and (b) different PN contents.

Table S1. Photovoltaic date of the PBZ-ClSi:IT-4F-based PSCs with (a) different D/A ratios and (b) different PN contents.

PBZ-ClSi:IT-4F	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE^{d} [%]
1.5:1	0.93	18.3 (17.4)	55.9	9.5 (9.2)
1:1	0.93	17.9 (17.1)	66.7	11.2 (11.0)
1:1^{a}	0.94	17.9 (17.2)	68.6	11.6 (11.3)
1:1^{b}	0.93	19.2 (18.3)	71.5	12.8 (12.5)

1:1[c]	0.93	17.2 (16.5)	71.1	11.4 (11.0)
1:1.5	0.93	17.3 (16.6)	67.1	10.8 (10.4)

[a] With 0.5% PN. [b] With 1% PN. [c] With 1.5% PN. [d] The average PCEs in parentheses from 20 devices.

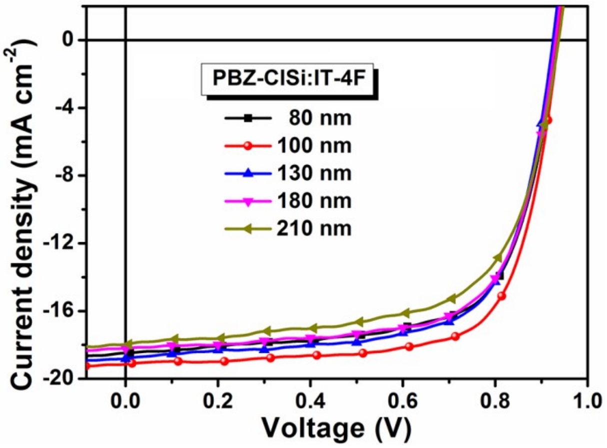

Fig. S5. The *J-V* curves of the PBZ-ClSi:IT-4F-based PSCs with different active layer thicknesses.

Table S2. Photovoltaic performances of the PBZ-ClSi:IT-4F-based PSCs with different active layer thicknesses under the illumination of AM 1.5G, 100 mW cm^{-2}.

Thickness [nm]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE[a] [%]
80	0.93	18.6	68.9	11.9 (11.6)
100	0.93	19.2	71.5	12.8 (12.6)
130	0.93	18.8	69.1	12.1 (11.7)
180	0.93	18.2	68.3	11.6 (11.1)
210	0.93	18.0	65.4	11.0 (10.4)

[a] The average PCE values in brackets from 10 devices.

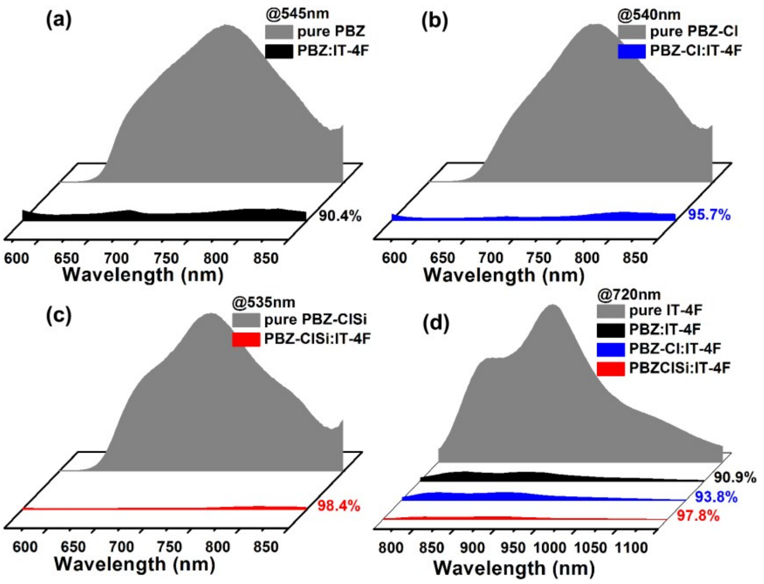

Fig. S6. The PL spectra of pure polymer and IT-4F films and the related blend films (excited at 545 nm for PBZ, 540 nm for PBZ-Cl, 535 nm for PBZ-ClSi, and 720 nm for IT-4F and the related blend films).

References

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