

Electronic Supplementary Information

Low boiling point solvent additive enables vacuum drying-free processed 230 nm thick PTB7-Th:PC₇₁BM active layer with more than 10% power conversion efficiency

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General Information

PTB7-Th is the product of 1-Material while PC₇₁BM is from Sigma-Aldrich. As measured by high temperature gel permeation chromatography (HT-GPC) at 150 °C with 1,2,4-trichlorobenzene as the eluent, the number-averaged molecular weight of 30.0 kg mol⁻¹ and polydispersity index of 2.6 were obtained for polymer PTB7-Th. Tapping-mode atomic force microscopy (AFM) images were obtained using a Nano Scope NS3A system (Digital Instrument) to observe the surface morphology of active layers of PTB7-Th/PC₇₁BM blends. Transmission electron microscopy (TEM) images were obtained using JEM-2100F with an accelerating voltage of 30 kV.

Device fabrication and characterization

Patterned indium tin oxide-coated glass substrate with a sheet resistance of 15-20 ohm/square were cleaned by a surfactant scrub, then underwent a wet-cleaning process inside an ultrasonic bath, beginning with acetone, detergent, deionized water, isopropanol and dried in vacuum

drying oven. After oxygen plasma treatment for 3 min, a 40 nm thick poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Clevios P AI4083) anode buffer layer was spin-coated on the ITO glass substrate and then dried by baking on a hot plate at 140 °C for 15 min. The PTB7-Th:PC₇₁BM solution was prepared by dissolving the polymer donor PTB7-Th and electron acceptor PC₇₁BM with a weight ratio of 1:1.5 or 1:2 in chlorobenzene (CB) without an additive or with 3% or 5% volume fraction of additives and was stirred on a hot plate at 50 °C for overnight. Subsequently, the active layers with different thickness were deposited on the top of PEDOT:PSS layer. The PFN solution in methanol was spin-casted on the active layer to form a thin interface layer. The thickness of the active layer is verified by a surface profilometer (Tencor, Alpha-500). Finally, a 100nm aluminum layer was thermally evaporated with a shadow mask at a cavity pressure of 2×10^{-6} . The overlapping area between the cathode and anode defined a pixel size of 0.058 cm². The thickness of the evaporated cathodes was monitored by a quartz crystal thickness/ratio monitor (Model: STM-100/MF, Sycon). Except for the deposition of the PEDOT:PSS layers, all the fabrication processes were carried out inside a controlled atmosphere of nitrogen dry-box (Braun GmbH) containing less than 0.1 ppm as for oxygen and moisture. The power conversion efficiencies of the resulting polymer solar cells were measured under 1 sun, AM 1.5G(air mass 1.5 global) spectrum from a solar simulator ((Japan, SAN-EI, XES-40S1) (100 mW/cm²). The current density-voltage (*J-V*) characteristics were recorded with a Keithley 2400 source unit.

Space-Charge Limited Current (SCLC) Measurement

Hole-only and electron-only devices were fabricated to measure the hole and electron mobilities of active layers using the space charge limited current (SCLC) method with hole-only device of ITO/PEDOT:PSS/PTB7-Th:PC₇₁BM/Au and electron-only device of ITO/Al/PTB7-Th:PC₇₁BM/Ca/Al. The mobilities (μ) were determined by fitting the dark current to the model of a single carrier SCLC, described by the equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$$

where J is the current, E is the effective electric field, ϵ_0 is the permittivity of free space, ϵ_r is the material relative permittivity, d is the thickness of the active layer, and V is the effective

voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

Transient Photovoltage (TPV) and Transient Photocurrent (TPC)

TPV and TPC of PSC devices were measured by ultrafast laser with a pulse width of 120 fs and low pulse energy. The laser pulses were generated from optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti:sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (SpectraPhysics Spitfire Ace). The transient signal was recorded by an oscilloscope (Tektronix TDS 3052C). During TPV measurements, the device was held at open circuit (100M Ω input impedance) under steady state conditions controlled by antinuous white light bias and a small pulsed perturbation of excess charge carriers was produced by the pulse laser (600 nm). The decay time (τ) was calculated by fitting a single exponential function to the transient photovoltage signal. TPC measurements were performed using a similar setup as for the TPV measurements. The device connected to the oscilloscope (50 Ω input impedance) under short circuited condition in dark.

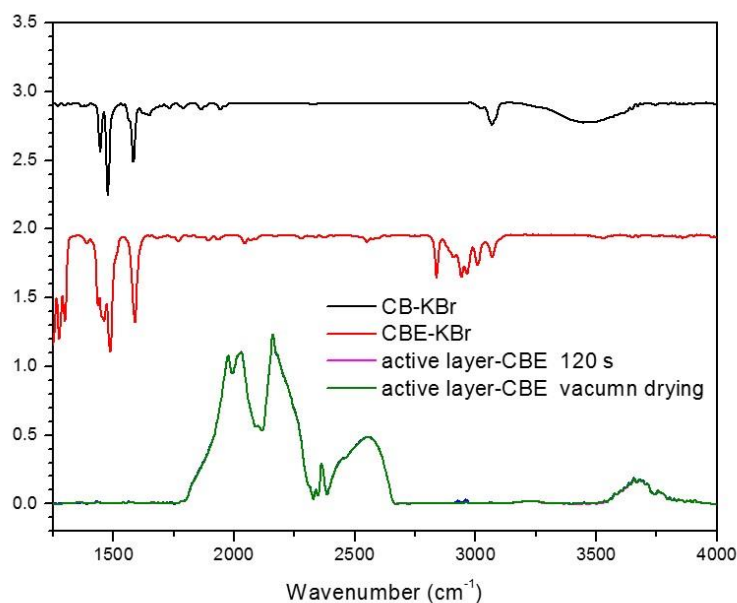


Fig. S1 IR spectra of chlorobenzene (CB) and *o*-chloroanisole (CBE) in KBr pellets as well as CBE-processed PTB7-Th:PC₇₁BM blend films after 2 min spin-coating at 1400 rpm and with additional vacuum drying for 3 h. The two blend films do not show signals from CB and CBE, indicating all of them are fully dried.

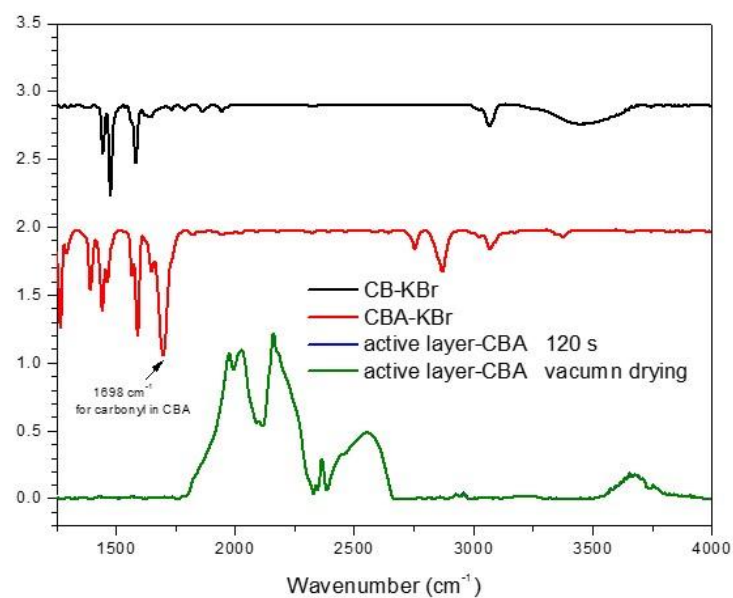


Fig. S2 IR spectra of chlorobenzene (CB) and *o*-chlorobenzaldehyde (CBA) in KBr pellets as well as CBA-processed PTB7-Th:PC₇₁BM blend films after 2 min spin-coating at 1400 rpm and with additional vacuum drying for 3 h. The two blend films do not show signals from CB and CBA, indicating all of them are fully dried.

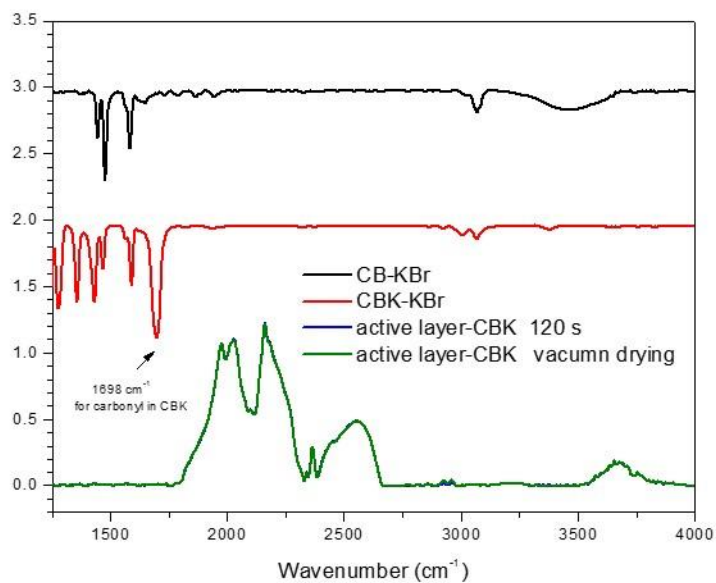


Fig. S3 IR spectra of chlorobenzene (CB) and *o*-chloroacetophenone (CBK) in KBr pellets as well as CBK-processed PTB7-Th:PC₇₁BM blend films after spin-coating at 1400 rpm for 2 min and with additional vacuum drying for 3 h. The two blend films do not show signals from CB and CBK, indicating all of them are fully dried.

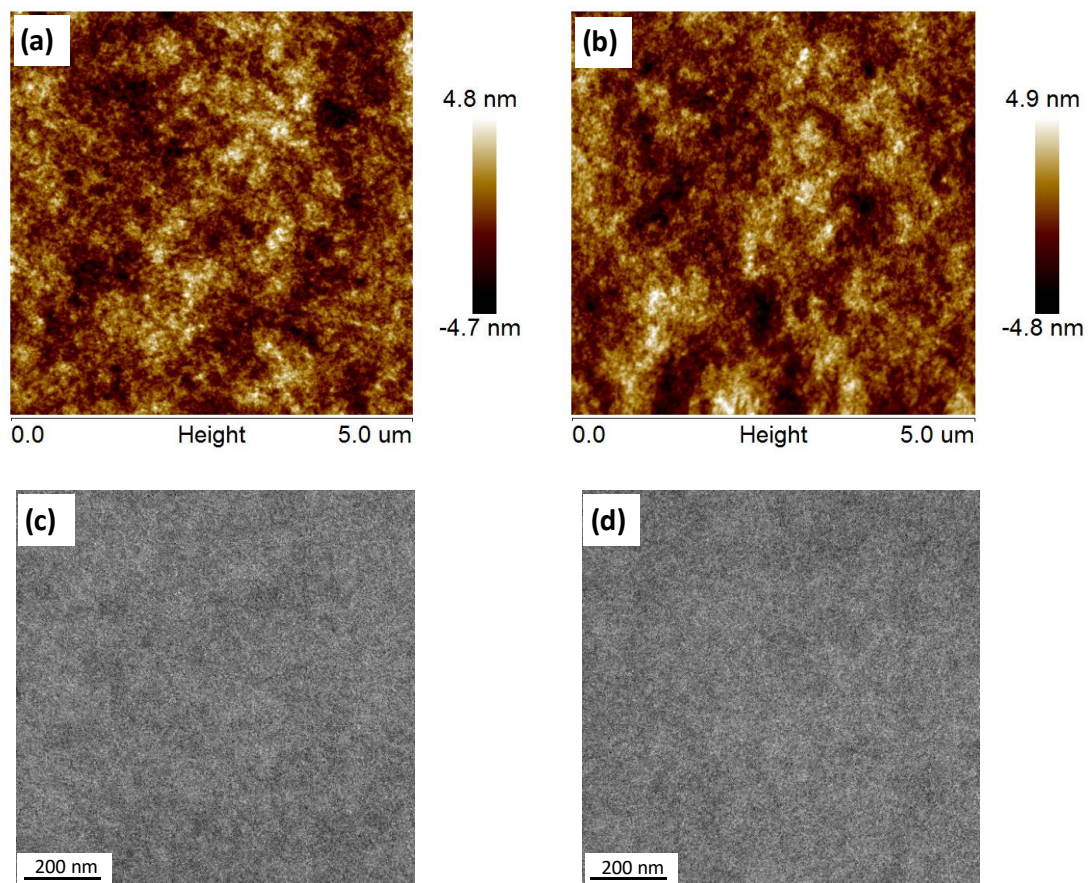


Fig. S4 (a,b) AFM images ($5 \times 5 \mu\text{m}^2$) for (a) CBA- and (b) CBK-processed 230 nm PTB7-Th:PC₇₁BM = 1:2 blend films. (c,d) TEM images for (c) CBA- and (d) CBK-processed 230 nm PTB7-Th:PC₇₁BM = 1:2 blend films.