
Supporting information

Binary Nonchlorinated and Nonaromatic Solvent-Processed PTB7:PC₇₁BM and PTB7-Th:PC₇₁BM Active Layers Showing Efficiency Comparable to that of Chlorobenzene in Organic Solar Cells

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Hansen solubility parameters (HSPs)^{1,2}

Hansen solubility parameters (HSPs) are widely used to correlate and predict the behavior of solvents. The starting point of the solubility parameter approach is due to Hildebrand, who introduced the cohesive energy density (CED)

$$\text{Cohesive energy density(CED)} = \frac{\Delta E}{V} = \frac{\Delta H_V - RT}{V_m} \quad (1)$$

Hansen has divided the Hildebrand total solubility parameter into three partial components δ_d , δ_p and δ_{hb} , respectively.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_{hb}^2 \quad (2)$$

Where δ_d is the dispersion Hansen solubility parameter, δ_p is the polar Hansen solubility parameter, δ_{hb} is the hydrogen-bonding Hansen solubility parameter.

The HSP coordinates of the solute are at the center of a sphere (spheroid) and the radius of the sphere, R_0 , indicates the maximum difference in affinity tolerable for

complete solution (or other given interaction criteria) to take place. The radius of a solute's sphere is defined through experimental solubility results from tests with a large number of solvents. Good solvents are within the sphere, and bad ones are outside of it. The distance between the solute and any solvent, or between any two materials, called Distance in Hansen space (R_a)

$$R_a^2 = 4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{hb1} - \delta_{hb2})^2 \quad (3)$$

where 1 and 2 refer to the solute and the solvent respectively, or any two different materials. A simple composite affinity parameter, the Relative Energy Difference (RED) number, has been defined according to Equation (5)

$$RED = \frac{R_a}{R_0} \quad (4)$$

RED becomes 0 if there is no energy difference. Good solvents have a RED number less than 1. Progressively poorer solvents have increasingly higher RED numbers.

Experimental

Materials and instrumentations

PTB7 and PTB7-Th was obtained from 1-materials, with number-averaged molecular weight of 60.2 and 30.0 kg mol⁻¹ and polydispersity index of 2.4 and 2.6, respectively. Chlorobenzene, 1,8-diiodooctane, and PC₇₁BM were purchased from Sigma-Aldrich. Poly[(9,9-dioctyl-2,7-fluorene)-alt-(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)] (PFN) was supplied by Derthon Optoelectronic Materials. Terpinolene (95%) was purchased from J&K Scientific. 1,4-Dioxane (99.8%) was obtained from Alfa Aesar.

The atomic force microscopy (AFM) measurements of the surface morphology of blend films were conducted on a NanoScope NS3A system (Digital Instrument). UV-vis absorption spectra were recorded on a HP 8453 spectrophotometer. Transmission electron microscopy (TEM) images were obtained by using a JEM 2100F Microscope.

Device fabrication and characterization

Bulk heterojunction polymer solar cells with conventional structure were fabricated with the configuration of ITO/PEDOT:PSS/active layer/PFN/Al. Patterned indium tin oxide (ITO)-coated glass with a sheet resistance of 15-20 ohm/square was cleaned by sequential ultrasonication in acetone and isopropanol (10 min). After treated with an oxygen plasma for 4 min, the ITO-coated glass substrates was spin-coated with poly(styrene sulfonate)-doped poly(ethylene-dioxythiophene) (PEDOT:PSS) (Bayer Baytron 4083) layer (40 nm) at 3000 rpm for 30 s, and annealed at 150 °C for 15 min in air and then transferred to a N₂-glovebox. To form an ultra-thin cathode interlayer, a 0.02% (w/v) PFN solution in methanol was spin-casted (2000 rpm for 30 s) on the top of the active layer (please see descriptions below).

For the inverted structure, device configuration is ITO/ZnO/PFN/active layer/MoO₃/Ag. The ZnO (obtained from stirring the solution of 1.0 g Zn(CH₃COO)₂·2H₂O in 10 mL ethylene glycol monomethyl ether and 277 μL ethylenediamine at 60 °C for 6 h) film (35nm) was spun onto the cleaned ITO at 3000 rpm for 30 s, which was annealed at 200 °C on a hot plate for 1 hour. And then the substrates were transferred to a N₂-glovebox and a 0.05% (w/v) PFN solution in

methanol was spin-casted (2000 rpm for 30 s) was deposited on the ZnO layer to form the ZnO/PFN bi-interlayer.

The active layer consisting of PTB7:PC₇₁BM (1:1.5) and PTB7-Th:PC₇₁BM (1:1.5) in DIOX, TPO:DIOX mixture, and CB was spin-coated with an approximate layer thickness of 90 nm. The used concentration for PTB7 or PTB7-Th was 10 mg/mL. 1,8-Diiodooctane of 5%, 5%, and 3% was utilized as solvent additive for DIOX, TPO:DIOX mixture, and CB, respectively. Active layers were kept in a transfer chamber under vacuum for overnight to remove the residual DIO. Al electrode (100 nm) was evaporated in a high-vacuum chamber with base pressure < 3×10⁻⁶ mbar through a shadow mask to define the active area (0.057 cm²) of the devices. The thickness of the active layer was verified by a surface profilometer (Tencor Alpha-500, USA).

The current density-voltage (*J-V*) characteristics were recorded with a Keithley 2400 source meter under 1 sun, AM 1.5G (air mass 1.5 global) spectrum from a solar simulator (Oriel model 91192, USA) set to 100 mW cm⁻². The external quantum efficiency (EQE) spectra were performed on a commercial EQE measurement system (Taiwan, Enlitech, QE-R3011). The light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cell.

Hole-only and electric-only devices were fabricated to measure the hole mobility and electric mobility using space-charge limited current (SCLC) method with a device structure of ITO/PEDOT:PSS/Active layer/MoO₃/Al and ITO/ZnO/Active layer/PFN/Al. The method to calculate the mobility could be found in literature.³

Table S1. Photovoltaic performances of conventional OSCs based on PTB7:PC₇₁BM active layers casted from DIOX:TPO (58:42) mixture with different DIO contents

DIO content (%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
1	12.00	0.73	39.79	3.48
3	14.81	0.75	64.49	7.16
5	15.36	0.75	65.94	7.60
7	14.99	0.75	61.63	6.93

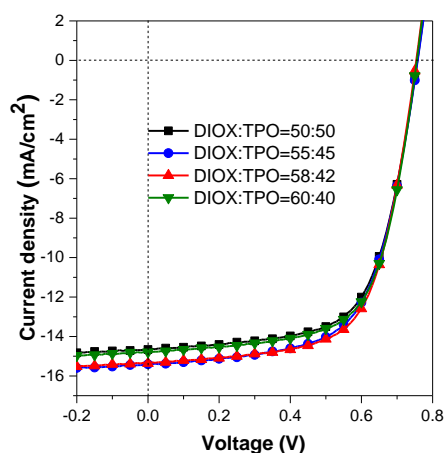


Figure S1. J - V characteristics for conventional OSCs based on PTB7:PC₇₁BM active layers casted from DIOX:TPO mixtures of different ratios.

Table S2. Photovoltaic performances of conventional OSCs based on PTB7:PC₇₁BM active layers casted from DIOX:TPO mixtures of different ratios

Solvent	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE ^a (%)
DIOX:TPO=50:50	14.66	0.76	64.99	7.24 (7.09)
DIOX:TPO=55:45	15.41	0.76	63.63	7.45 (7.28)
DIOX:TPO=58:42	15.36	0.75	65.94	7.60 (7.45)
DIOX:TPO=60:40	14.79	0.76	65.52	7.36 (7.18)

Table S3. The SCLC hole and electron mobilities of the CB and DIOX:TPO (58:42) mixture processed PTB7:PC₇₁BM and PTB7-Th:PC₇₁BM blend films

polymer	solvent	μ_h ($10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)	μ_e ($10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)	μ_h/μ_e
PTB7	CB	2.33	1.41	1.65
PTB7	DIOX:TPO	2.26	1.45	1.55
PTB7-Th	CB	1.93	1.24	1.55
PTB7-Th	DIOX:TPO	1.99	1.42	1.40

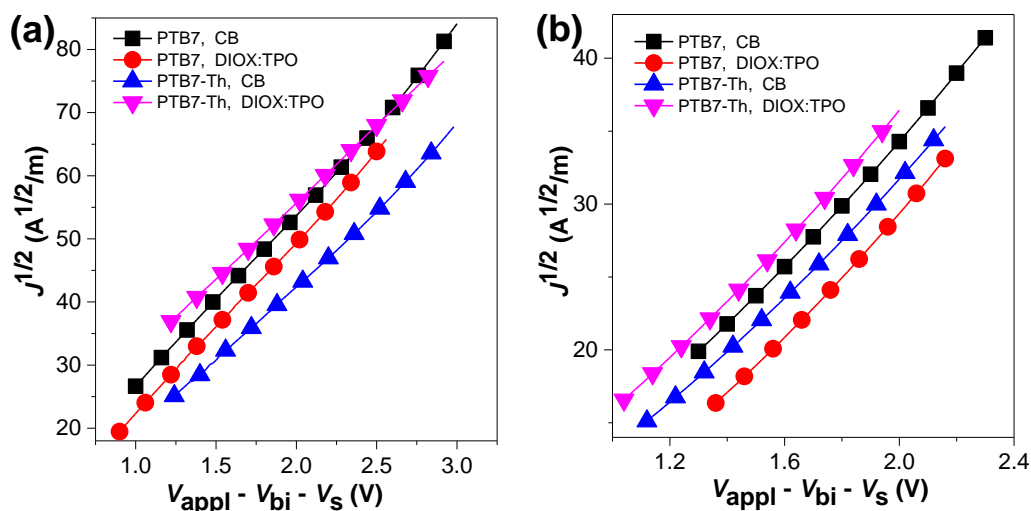


Figure S2. Experimental (symbols) and calculated (solid lines) $J^{1/2}$ - V characteristics of (a) hole-only and (b) electron-only devices.

Reference

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