

SUPPORTING INFORMATION

Fullerene-Free Polymer Solar Cells Processed from Non-Halogenated Solvents in Air with PCE of 4.8%

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Materials

All materials were purchased from Aldrich Chemicals and used as received. Polymer **PTB7-Th** was purchased from One-Material and used as received. The energy levels of **PTB7-Th** were estimated in house, in an identical fashion to **tPDI-Hex**, using solution cyclic voltammetry.

Equipment

UV-vis absorption measurements were carried out on an Agilent Technologies Cary 60 UV-vis spectrometer at room temperature. The photoluminescence spectra measurements were recorded using an Agilent Technologies Cary Eclipse fluorescence spectrophotometer at room temperature. Atomic force microscopy (AFM) images were obtained using a TT2-AFM (AFM workshop) in the tapping mode and a WSxM software.

Experimental Section

Solar Cells Fabrication and Testing: Solar cells were fabricated on ITO-coated glass substrates, which were first cleaned by sequentially ultra-sonicating detergent and de-ionized water, acetone, and then isopropanol before use. ITO substrates were first pretreated UV-ozone for 30 minutes, then, ZnO precursor solution was spin-cast onto the ITO substrate at a speed of 4000 rpm and then annealed at 200 °C in air for 1 hour. Active layer solutions (**PTB7-Th:tPDI-Hex**

weight ratios 2:3 or 3:7) were prepared in chloroform (CF), 2-methyl tetrahydrofuran (2Me-THF), *o*-Xylene, or 1,2,4-trimethylbenzene (TMB) without any additives. The total concentration of mixed **PTB7-Th:tPDI-Hex** is 10 mg ml⁻¹ was for CF, 2Me-THF, and *o*-Xylene solvents and 15 mg 10 mg ml⁻¹ for TMB. For CF, 2Me-THF, and TMB solvents, the films giving best device PCE were spin-coated at room temperature at 1500 rpm in air. Active layers from *o*-Xylene with best device PCE were spin-coated at 600 rpm. The substrates were then kept in an N₂ atmosphere glovebox overnight before evaporating MoO_x and Ag. The evaporation of 10 nm of MoO_x followed by 100 nm of Ag were thermally deposited under vacuum (4x10⁻⁶ Torr). Current density-voltage (J-V) characteristics were measured using a Keithley 2420 Source Measure Unit. Solar cell performance used an Air Mass 1.5 Global (AM 1.5G) Solar Simulator (Newport, Model 92251A-1000) with an irradiation intensity of 100 mW cm⁻², which was measured by a calibrated silicon solar cell and a readout meter (Newport, Model 91150V). EQE spectra were measured by using a QEX7 Solar Cell Spectral Response/QE/IPCE Measurement System (PV Measurement, Model QEX7) with an optical lens to focus the light into an area about 0.04 cm², smaller than the dot cell. The silicon photodiode was used to calibration of the EQE measurement system in the wavelength range from 300 to 1100 nm.

Supporting Figures

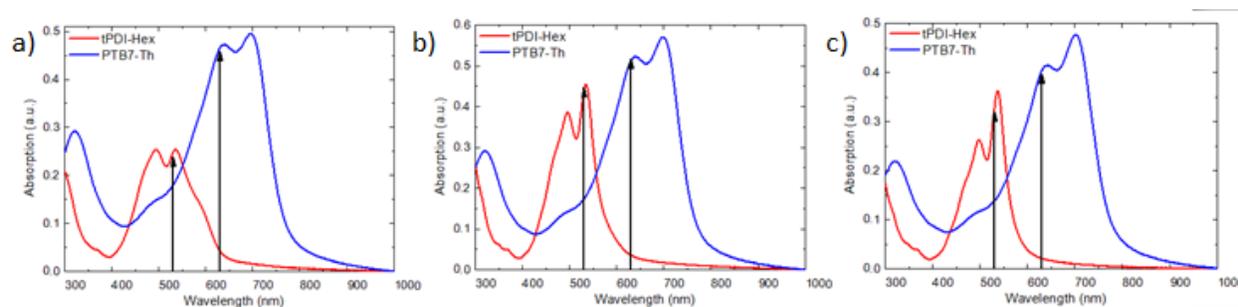


Figure 1SI. a) Absorption spectra of **PTB7-Th** and **tPDI-Hex** films obtained from CF, b) 2Me-THF and c) *o*-Xylene (the arrows indicate the length of the excitation waves 530 and 630 nm).

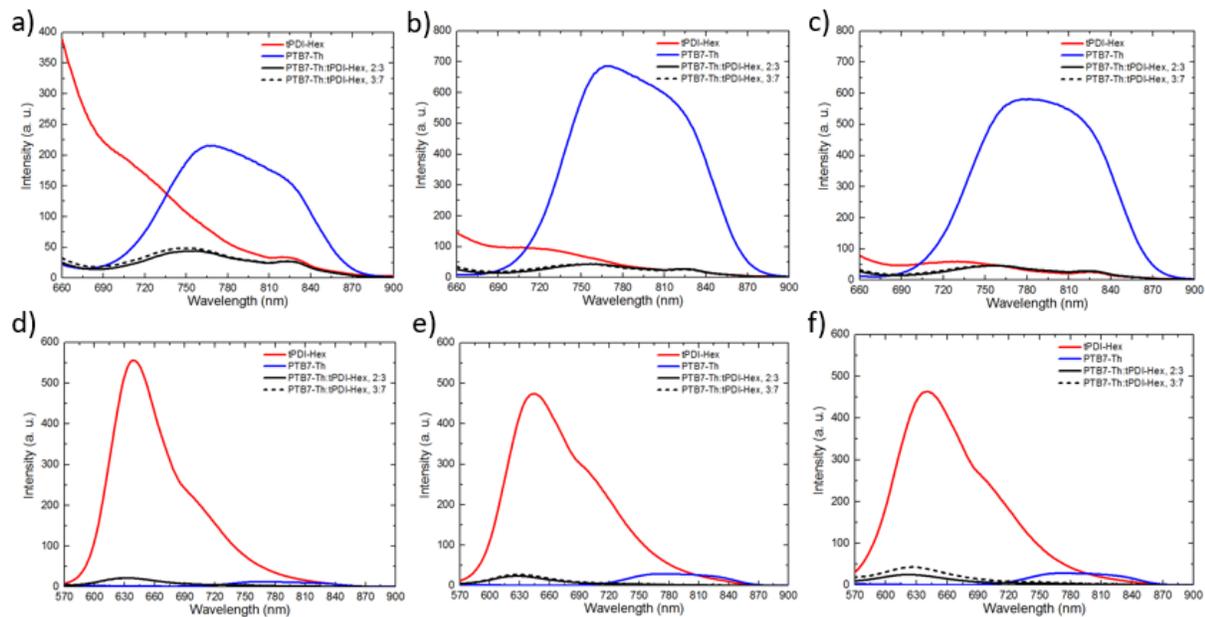


Figure 2SI. **a)** The normalized photoluminescence spectra of **tPDI-Hex**, **PTB7-Th** and BHJ films with 2:3 and 3:7 ratios obtained from CF, **b)** 2Me-THF and **c)** *o*-Xylene at excitation wavelength 630 nm. **d)** The normalized photoluminescence spectra of **tPDI-Hex**, **PTB7-Th** and BHJ films with 2:3 and 3:7 ratios obtained from CF, **e)** 2Me-THF and **f)** *o*-Xylene at excitation wavelength 530 nm.

Table S1. Solvent Comparison Table.

Solvent	Chemical Structure	^a Boiling Point (°C)	^b Dipole Moment (Debye)	^a Specific Gravity (Water = 1)	^a Vapor Pressure (@20C, kPa)	List Price (Aldrich Cat. No., \$ CAD)	^a Toxicity (LD50, mg/kg, rat)	^a Advantages	^a Disadvantages
Chloroform		61	1.01	1.48	21.1	(C2432-1L, 80 \$)	695	Canonical use, Dissolves many organic compounds.	Volatile, Halogenated Solvent. Toxic, Carcinogen, Mutagen
O-Xylene		144	0.62	0.88	0.90	(294780-2L, 199 \$)	1364	High B.P, non-halogenated, Biodegradable	Flammable, Carcinogen, Teratogen
2-Me-THF		80	^c 1.38	0.86	20.7*	(414247-1L, 211.5 \$)	>2000	^c Derived from Biomass. Biodegradable	Flammable, Chronic Health effects.
1,2,4-Trimethyl Benzene		169-171	^d 0.41	0.88	2.80	(T73601-2L, 116.50 \$)	3280	High BP, non-halogenated	Flammable, Toxic

^a Data used in table taken from Materials Safety Data Sheets (MSDS) provided by chemical vendors. * = data @ 25C.

^b Data taken from: CRC Handbook of Chemistry and Physics (85th Edition).

^c Data taken from: *Organic Process Research & Development* **2007** 11 (1), 156-159.

^d Data taken from: *Phys. Chem.*, 1953, 57 (5), pp 538–540.

Note: Halogenated solvents have known impacts on the ozone layer and can be difficult to dispose of, due to the formation of halo-acids upon burning. ¹⁻³

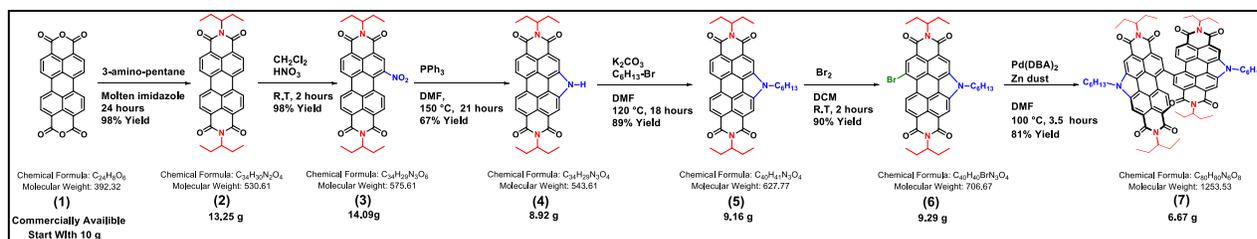


Figure 3SI: Synthetic route towards **tPDI-Hex** (compound **7**). Yields are assumed from a previous report for the purpose of performing a rough ‘cost analysis’ for the acceptor **tPDI-Hex** (**7**).⁴ Starting with 10 g of the commercially available anhydride (**1**) and assuming the reported yields, 6.67 g of (**7**) can be obtained. Full synthetic details can be found in a previous publication from our group.⁴

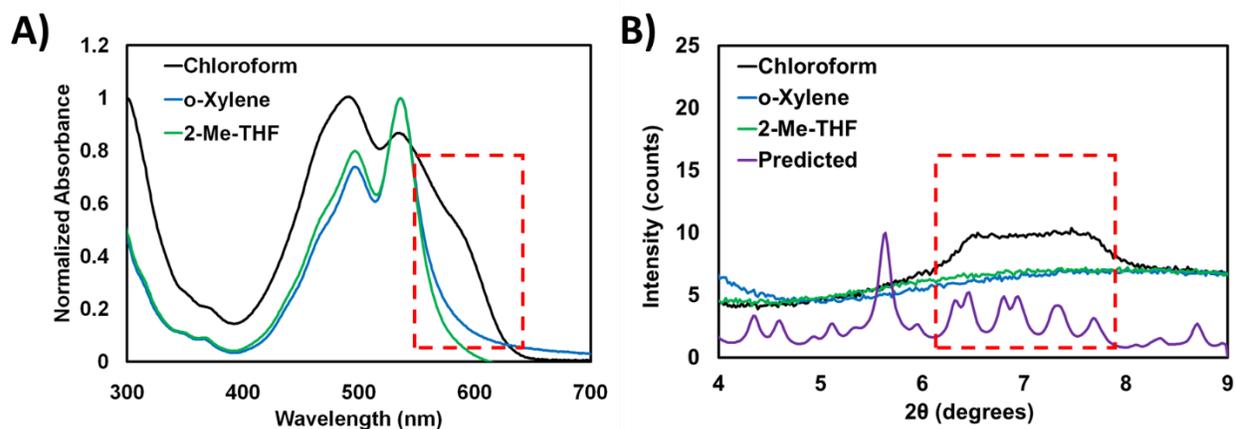


Figure 4SI: A) Optical absorption profiles of thin films of **tPDI-Hex** spin-cast from different solvents. All films were cast from 10 mg/mL solutions at 1500 rpm. The low energy shoulder that appears when cast from chloroform is highlighted using a red box. This feature is only visible in films of **tPDI-Hex** cast from chloroform, leading to the assertion that a different film morphology is attained when using this solvent. **B)** X-ray diffraction patterns of **tPDI-Hex** films. Films were drop-cast onto clean glass slides from different solvents as 10 mg/ml solutions and dried in air. The solvents used were: chloroform, *o*-Xylene, 2-Me-THF. All X-ray diffraction experiments were performed on a PROTO AXRD Benchtop Powder Diffractometer using θ -2 θ scans and Cu K- α radiation. Predicted powder pattern was generated from the previously reported crystal structure of **tPDI-Hex**.⁴ It has been previously reported in the literature that the light absorptive properties of PDI molecules may become dramatically changed upon aggregation.^{5,6} Taken together, the X-Ray data and UV-Visible absorption profiles of thin films provide qualitative evidence of a difference in morphology for films of **tPDI-Hex** cast from chloroform.

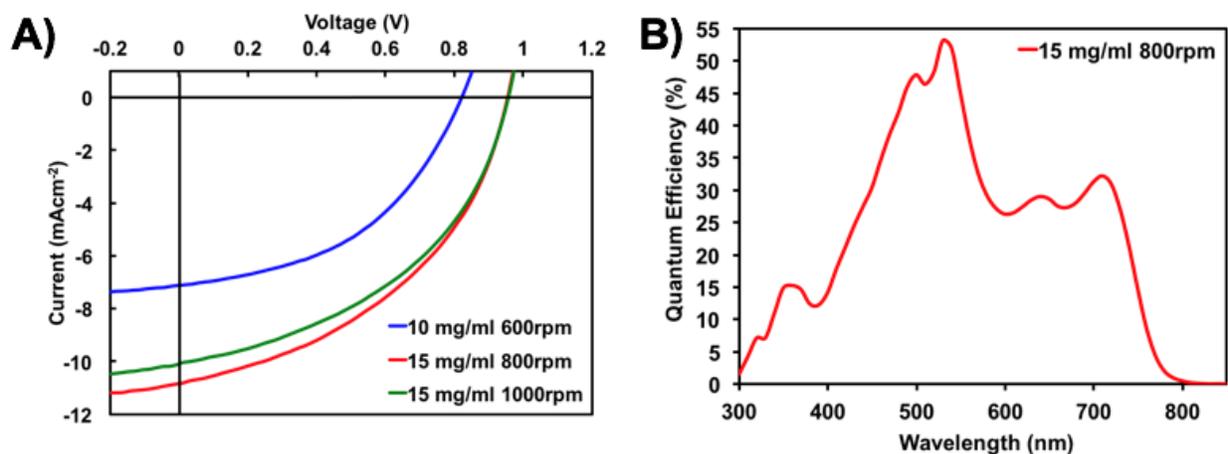


Figure 5SI: **A)** J-V characteristics of OSCs with an inverted structure based on **PTB7-Th:tPDI-Hex** blend films obtained from 1,2,4-Trimethyl Benzene (**TMB**) at 3:7 donor/acceptor ratios. Active layers were applied from the **TMB** at a total concentration of 10 and 15 mg/ml and at spin speeds of 600 and 800 or 1000rpm, respectively. OSC parameters are shown in the **Table S3**. The **PTB7-Th:tPDI-Hex** solar cell showed PCE of 4.6%, obtained at a concentration of 15 mg/ml, and 800 rpm. **B)** EQE spectrum of the best OSC with an inverted structure based on **PTB7-Th:tPDI-Hex** blend films obtained from chloroform **TMB** at 3:7 donor/acceptor ratios.

Table S3. Summary of device parameters of OSCs with an inverted structure based on **PTB7 Th:tPDI Hex** blend films obtained from **TMB** without additive or annealing at 3:7 donor/acceptor ratios under AM 1.5G illumination at 100 mW cm⁻².

Parameters	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	R_s [Ω cm ²]	R_{sh} [Ω cm ²]
10mg/ml, 600rpm	0.82	7.20	46.3	2.69	33.3	625.2
15mg/ml, 800rpm	0.95	10.78	44.6	4.58	16.6	392.9
15mg/ml, 1000rpm	0.95	10.08	45.2	4.35	18.9	411.8

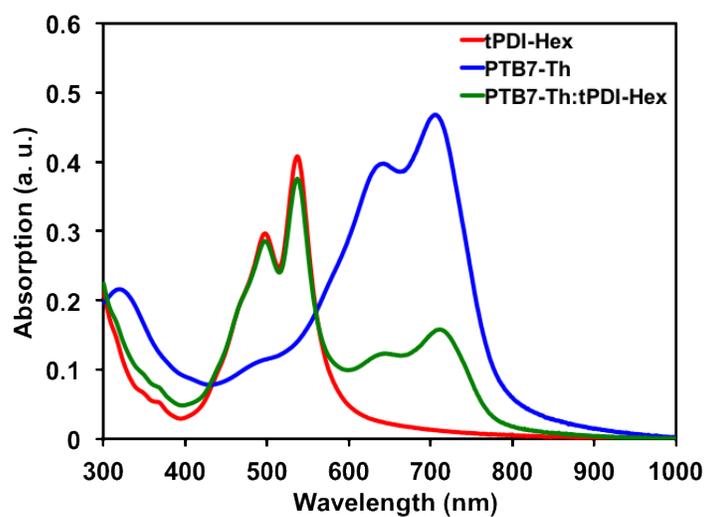


Figure 6SI: Optical absorption spectra of the **PTB7-Th** donor, the **tPDI-Hex** acceptor and the **PTB7-Th:tPDI-Hex** active layer obtained from **TMB** at 3:7 donor/acceptor ratios (15mg/ml, 800rpm, device PCE = 4.6%)

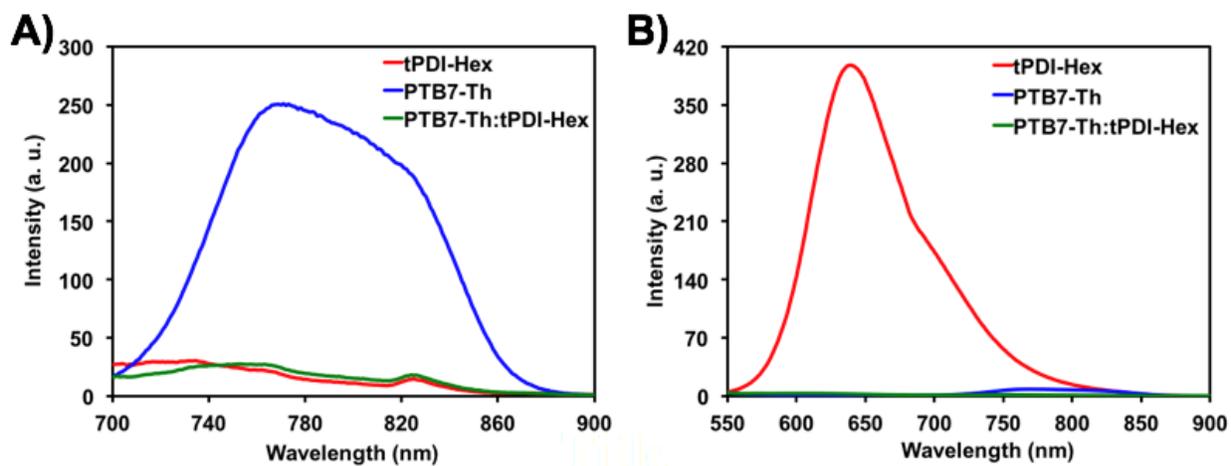


Figure 7SI: A) The photoluminescence spectra of **tPDI-Hex**, **PTB7-Th** and BHJ films with 3:7 ratios (15mg/ml, 800rpm, device PCE = 4.6%) obtained from **TMB** at excitation wavelength 630 nm. **B)** The photoluminescence spectra of **tPDI-Hex**, **PTB7-Th** and BHJ films with 3:7 ratios obtained from **TMB** at excitation wavelength 530 nm.

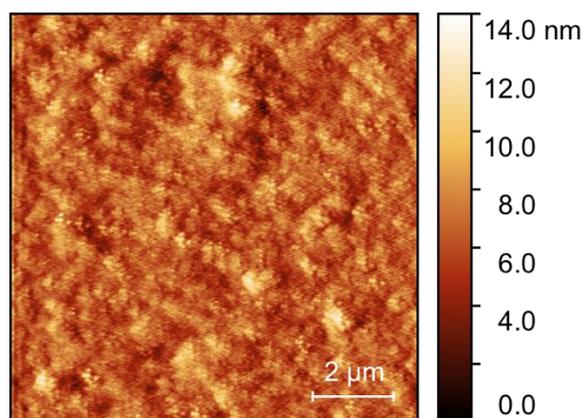


Figure 8SI: The non-contact AFM surface scan (size: 10x10 μm) of the **PTB7-Th:tPDI-Hex** film with 3:7 ratio obtained from the **TMB** (15mg/ml, 800rpm, device PCE = 4.6%) (RMS = 1.44 nm).

Table S4. Summary of device parameters of OSCs with an inverted structure based on **PTB7 Th:tPDI Hex** blend films obtained from CF, 2Me-THF and o-Xylene without additive or annealing at different donor/acceptor ratios under AM 1.5G illumination at 100 mW cm⁻². This table is different from Table 1 as it includes the calculated series and shunt resistance data.

Solvent	PTB7-Th:tPDI-Hex [wt/wt]	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%]	R_s [Ω cm ²]	R_{sh} [Ω cm ²]
CF	2:3	0.98	11.29	43.1	4.75	19.3	296.7
CF	3:7	0.97	10.83	42.2	4.44	19.9	286.0
2Me-THF	2:3	0.91	12.30	41.2	4.65	16.4	222.5
2Me-THF	3:7	0.94	11.63	43.7	4.78	15.3	313.8
o-Xylene	2:3	0.93	10.88	46.8	4.73	13.1	345.1
o-Xylene	3:7	0.95	10.61	50.0	4.81	12.4	391.9

References:

1. D. J. Burke and D. J. Lipomi, *Energy Environ. Sci.*, 2013, **6**, 2053–2066.
2. W.-Y. Lee, G. Giri, Y. Diao, C. J. Tassone, J. R. Matthews, M. L. Sorensen, S. C. B. Mannsfeld, W.-C. Chen, H. H. Fong, J. B.-H. Tok, M. F. Toney, M. He and Z. Bao, *Adv. Funct. Mater.*, 2014, **24**, 3524–3534.
3. V. Ramanathan, *Science*, 1975, **190**, 50.
4. A. D. Hendsbee, J.-P. Sun, W. K. Law, H. Yan, I. G. Hill, D. M. Spasyuk and G. C. Welch, *Chem. Mater.*, 2016, **28**, 7098–7109.
5. G. Klebe, F. Graser, E. Hädicke and J. Berndt, *Acta Crystallogr. Sect. B*, 1989, **45**, 69–77.
6. Z. Chen, V. Stepanenko, V. Dehm, P. Prins, L. D. A. Siebbeles, J. Seibt, P. Marquetand, V. Engel and F. Würthner, *Chem. – Eur. J.*, 2007, **13**, 436–449.