

Supporting Information

Role of trace impurities in the photovoltaic performance of solution processed small molecule bulk heterojunction solar cells

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Materials and Methods: All synthetic and characterization protocols have been previously reported.¹

Experimental:

Chemical Purification: ***p*-DTS(PTTh₂)₂** was prepared as previously reported.¹ Removal of the **(MePT)DTS(PTTh₂)** side product was achieved by vigorously stirring a slurry of contaminated ***p*-DTS(PTTh₂)₂** in a hexanes:methanol (50:50) mixture at room temperature, overnight (**(MePT)DTS(PTTh₂)** is extracted into the hexanes phase). The pure ***p*-DTS(PTTh₂)₂** was collected by filtration and washed with methanol and acetone and dried under vacuum. Absolute purity was determined by solution NMR spectroscopy and Mass Spectrometry.

Device preparation: The solar cells were fabricated on indium-tin oxide coated glass on which Molybdenum oxide (MoO_x) was thermally evaporated at a rate of 0.1 Å/s under a vacuum of about 1×10^{-6} torr. The thickness of MoO_x film was determined to be 9 nm. Subsequently, blends films of [6,6]-phenyl C71 butyric acid methyl ester

(PC₇₀BM) and *p*-DTS(PTTh₂)₂ were cast from a solution in the *p*-DTS(PTTh₂)₂:PC₇₀BM ratios of 7:3 in chlorobenzene solvent (total solids concentration of 40 mg/ml). BHJ films were annealed at 70°C for 10 minutes to remove any residual solvents. The devices were completed after deposition of the top aluminum electrode (device area of about 0.196 cm²). Devices were encapsulated for testing in air with a UV-curable epoxy and covered with a glass slide.

Transistor fabrication and characterization: Bottom-gate, gold bottom-contact organic field effect transistors (FETs) were fabricated where thin films of the semiconducting molecules (0.5wt% in chloroform) are spun coated onto heavily doped n-type silicon substrates with a 200 nm SiO₂ dielectric layer. The SiO₂ layer was pre-treated with octadecyltrichlorosilane. The semiconducting films were annealed at 70 °C for 10 min to remove the residual solvents. All devices have channel length of 20 μm and width of 1000 μm. Electrical characterization of the FETs was performed using a semiconductor parametric analyzer (Keithley 4200). All the processings and device characterization were performed in nitrogen filled glove box.

Device testing: J-V curves were recorded using an automated LabView computer program controlling a Keithley 2400 Sourcemeter. The devices were characterized using a Newport Air Mass 1.5 Global (AM 1.5G) full spectrum solar simulator with an irradiation intensity of 100 mW/cm². Intensity dependence studies were done using a set of neutral density filters, allowing a range of intensity from 2 mW/cm² to 100 mW/cm². IPCE spectra were measured by using a QE7 Solar Cell QE measurement system (PV measurements, Inc.). The background illumination during IPCE measurements was done

using a white Light Emitting Diode (LED), the intensity of which was controlled by the bias current, giving an intensity of 66.85 mW/cm².

Absorption spectra: The blend films were deposited on quartz substrates (~170-180nm thick) and film absorption were measured in transmission geometry using Beckman Coulter UV-visible spectrophotometer.

Transient absorption spectroscopy: Blended films were prepared as described above except they were cast onto sapphire discs and placed under rough vacuum for more than 12 hours before the measurements were taken. The transient absorption measurements were collected in the standard pump-probe setup in which the time delay between a pump pulse and a probe pulse can be varied through the use of a variable delay stage. The wavelength of the pump pulse is 400 nm and has a temporal width of 100 fs. It is generated by frequency doubling a titanium sapphire laser pumped by a Nd:YAG (Spectra Physics). The probe pulse is a white light continuum generated by focusing an 800 nm pulse into a sapphire disc. The broad continuum contains temporal chirp for which spectra are corrected during data processing. The spectrometer output is a series of spectra, one for each time delay. The dynamic traces of Figure 6 were made by integrating each spectrum from 850-1000 nm and plotting the result versus time.

TEM characterization: TEM characterization was performed on a FEI Titan operating at 300 kV equipped with a field emission gun on thin active layers (~100 nm) films spin cast on ITO/MoO_x substrates. More than a day after casting, active layers were submerged in DI water (10 min) and floated onto the air/water interface. Films were picked up ultra-thin carbon with lacy support films (Ted Pella). Imaging of the in-plane stacking was performed under defocus (about -1 μm) under approximate parallel

illumination; the first maximum of the microscope CTF easily covered the width of the in-plane peak allowing good representation of the lattice planes. Specimen damage – causing densification and movement of the sample – was the limiting factor and a low-dose imaging technique was adopted. First, the sample was allowed to mechanically stabilize (from 1 to several minutes). Stability was determined by the azimuthal uniformity of the Fourier transformed image in the sacrificial region. Next, the beam was shifted off the optical axis electronically to an undamaged region of the sample and, finally, an image was immediately taken. About 150 (50) images were taken for the pure (impure) sample. We note that sample with large crystals may have crystals even larger than imaged due to beam induced motion/bending. Full images of the pure and impure *p*-DTS(PTTh₂)₂:PC₇₀BM blend films with 0.25% v/v DIO are shown in Figures S6 and S7, respectively. For comparative purposes, a full image of the pure *p*-DTS(PTTh₂)₂:PC₇₀BM blend film with 0.60% v/v DIO is shown in Figure S8. The crystals are substantially larger than those found in the other devices and show a low PCE of 3.2%.¹ The lacy carbon substrate is visible to some degree in all of the images.

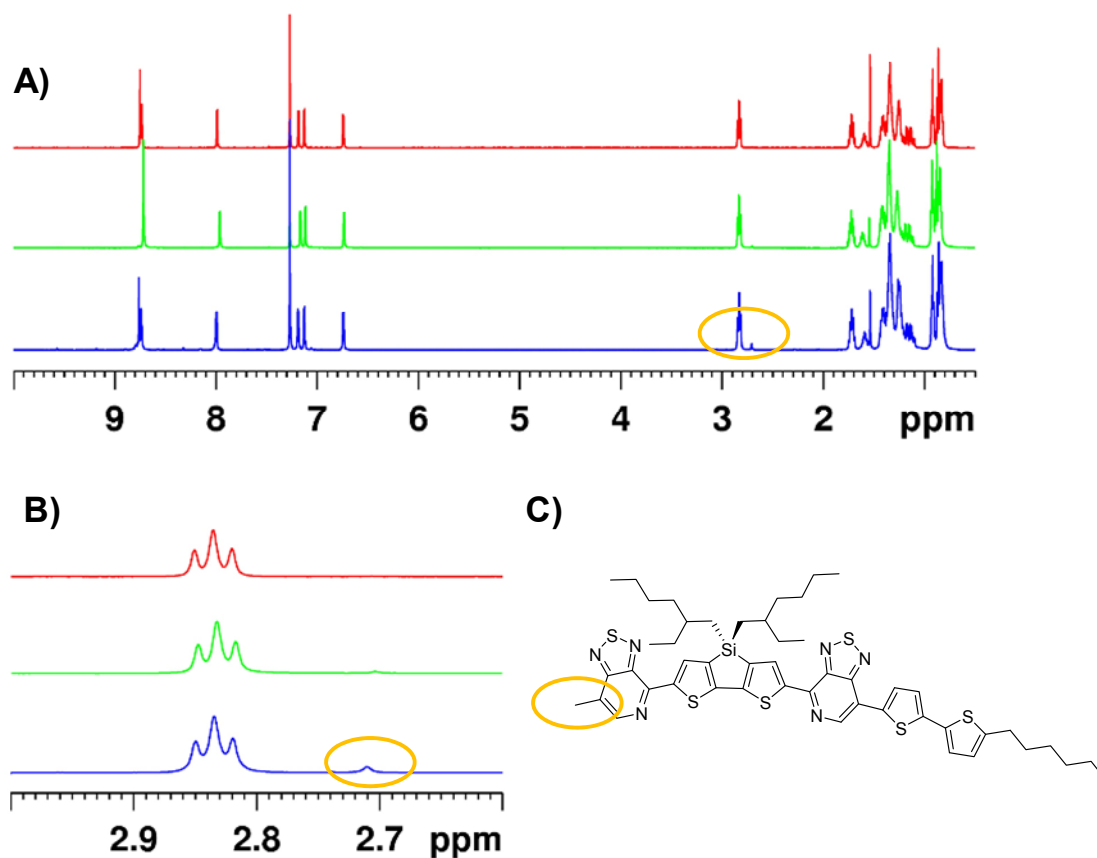


Figure S1. A) Full B) Expanded ^1H NMR spectra of $p\text{-DTS}(\text{PTTh}_2)_2$ in CHCl_3 (Slight chemical shift difference in the aromatic proton resonances attributed to concentration effects). Red Trace is for pure sample 1 that gives $>6\%$ PCE. Green trace is for sample 2 contaminated with small amounts $(\text{MePT})\text{DTS}(\text{PTTh}_2)$ and gives PCE = 3% . Blue trace is for sample 3 that was synthesized at 175°C and approximately 2 mol % $(\text{MePT})\text{DTS}(\text{PTTh}_2)$ as determined via integration of the ^1H NMR peaks (vide infra). Resonance at $\delta 2.83$ ppm attributed to the hexyl CH_2 adjacent the terminal thiophene unit. Resonance at $\delta 2.71$ ppm in the blue trace attributed the terminal PT methyl group (circled in orange) associated with $(\text{MePT})\text{DTS}(\text{PTTh}_2)$. C) Structure of $(\text{MePT})\text{DTS}(\text{PTTh}_2)$.

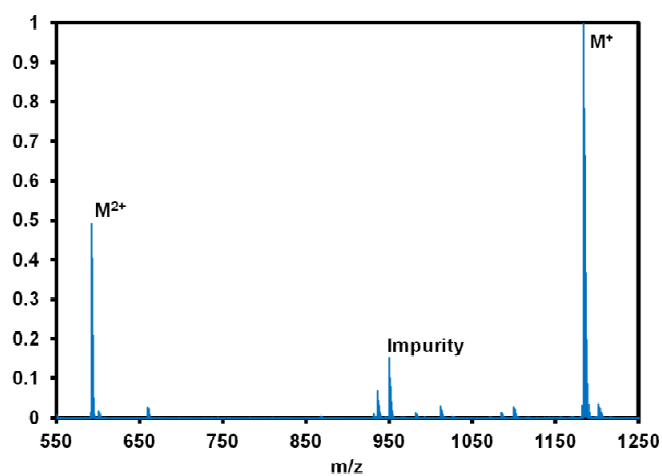


Figure S2. Low resolution field desorption LRFD mass spectra of *p*-DTS(PTTh₂)₂ sample 3 that was synthesized at 175 °C and contains approximately 2 mol % (MePT)DTS(PTTh₂). Shows DTS(PTTh₂)₂ M⁺ ion and M²⁺ with m/z = 1184 and m/z = 592, respectively. Shows DTS(PTTh₂)₂ fragmentation peak with m/z = 936. Shows M⁺ ion with m/z = 950 for (MePT)DTS(PTTh₂).

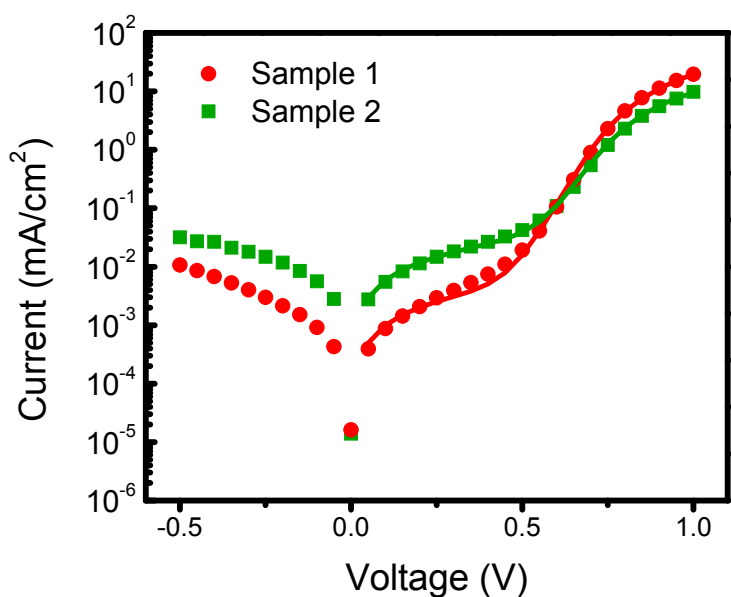


Figure S3. Dark current density vs. voltage for *p*-DTS(PTTh₂)₂:PC₇₁BM device comprising pure and impure *p*-DTS(PTTh₂)₂, sample 1 and 2 respectively. The solid lines are fits to the Shockley diode equation.

Table S1 Fit parameters for the dark J-V curves

	J_0 (mA/cm ²)	n	R_s (Ω)	R_{sh} (Ω)	RMS error
pure <i>p</i> -DTS(PTTh ₂) ₂ :PC ₇₀ BM	9.0x10 ⁻¹¹	1.65	9.2	1.0x10 ⁵	0.159
Impure <i>p</i> -DTS(PTTh ₂) ₂ :PC ₇₀ BM	2.0x10 ⁻¹⁰	1.80	18.1	1.70x10 ⁴	0.057

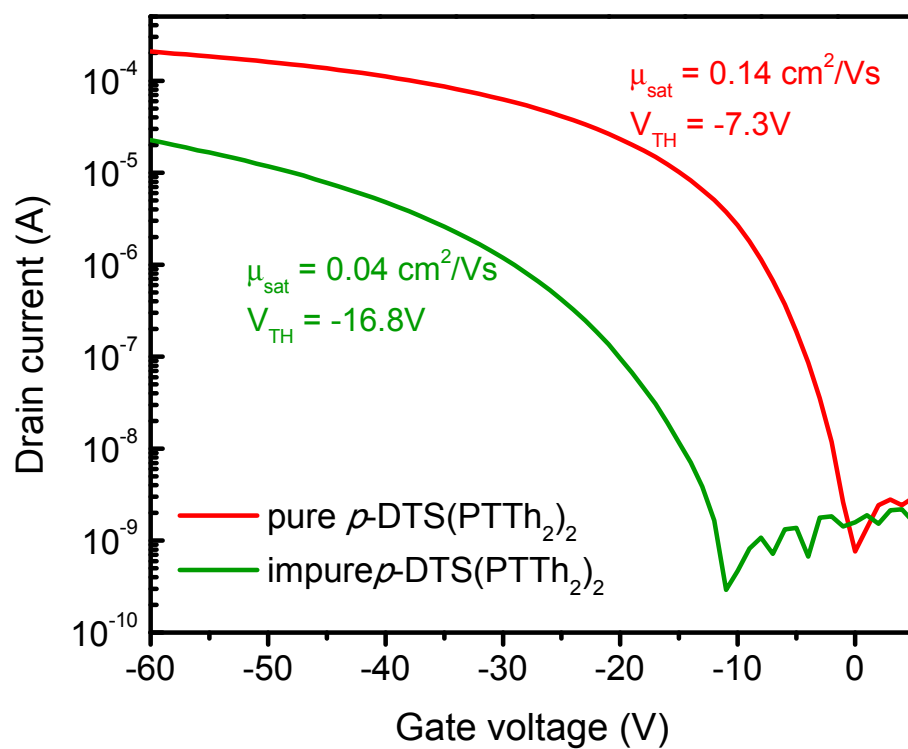


Figure S4. Transfer characteristics in bottom-gate/bottom contact field effect transistor using pure and impure $p\text{-DTS(PTTh}_2)_2$. The applied drain-source voltage is -60V. The channel length and width was 1000 μm and 20 μm respectively.

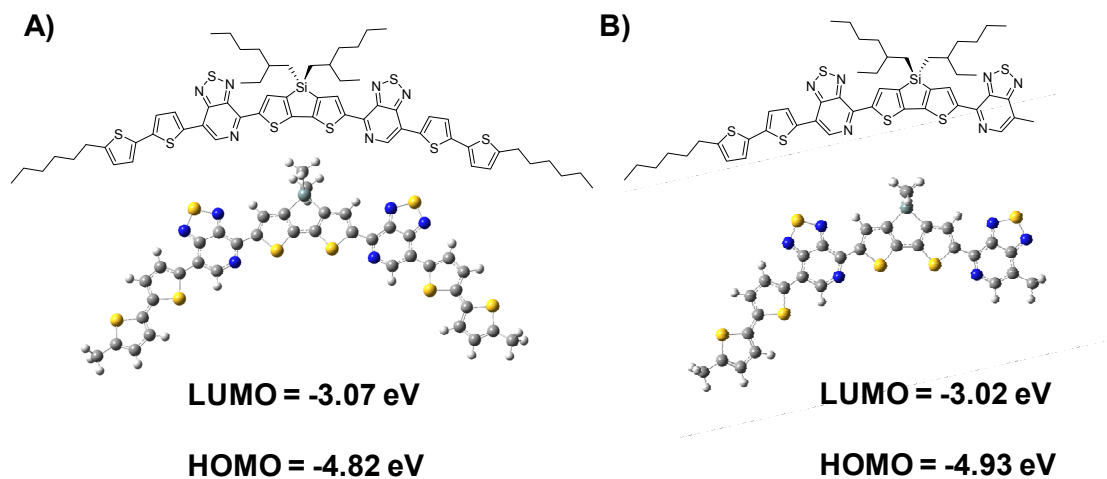


Figure S5. Gas-phase DFT optimized structures at the B3LYP/6-31G(d,p) level of theory. A) *p*-DTS(PTTh₂)₂ and B) (MePT)DTS(PTTh₂). Calculations show both the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) energy levels are similar for both materials.

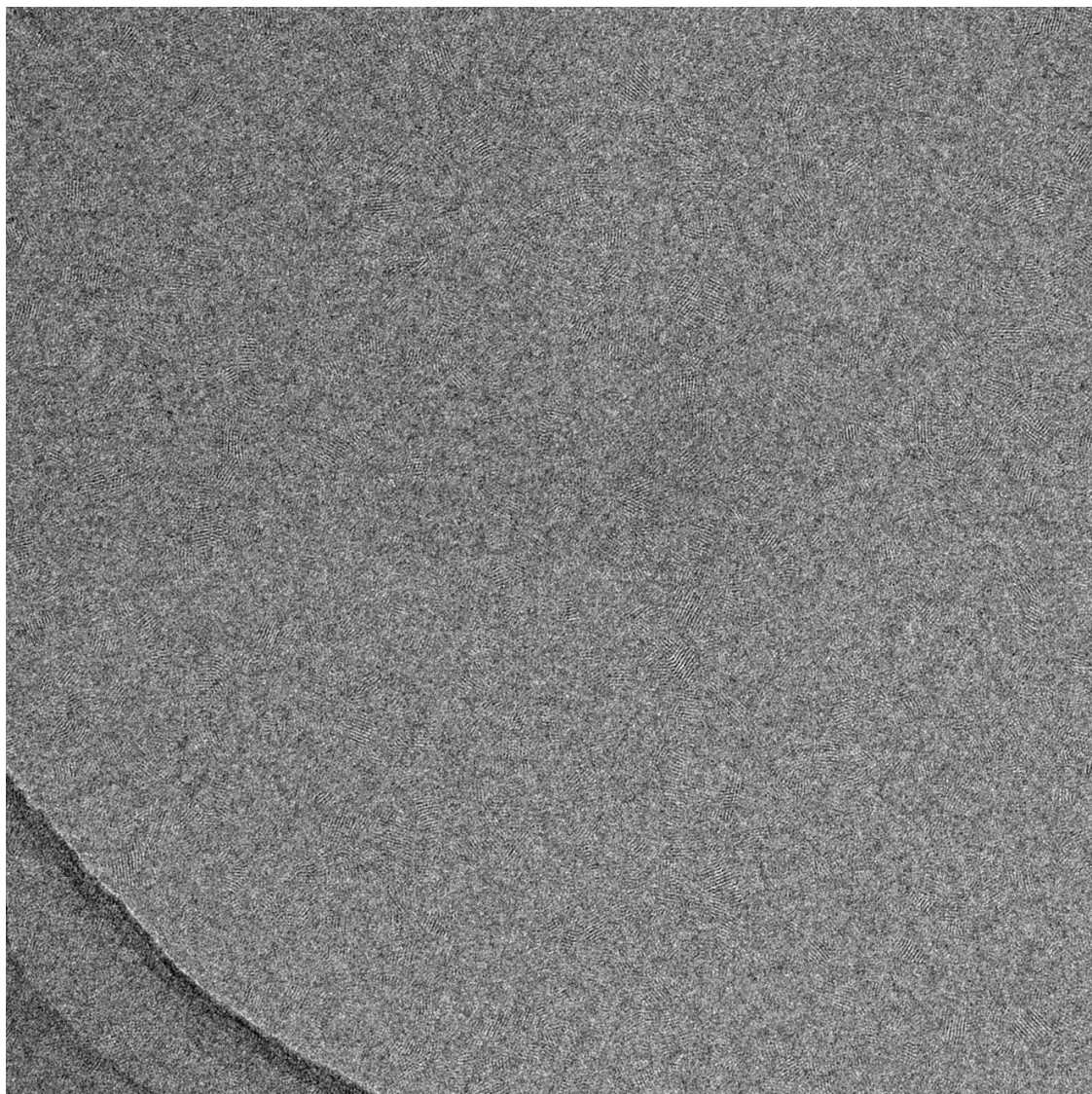


Figure S6. Larger image of pure *p*-DTS(PTTh₂)₂:PC₇₀BM blend films cast with 0.25% v/v DIO. Image is 650 nm on a side.

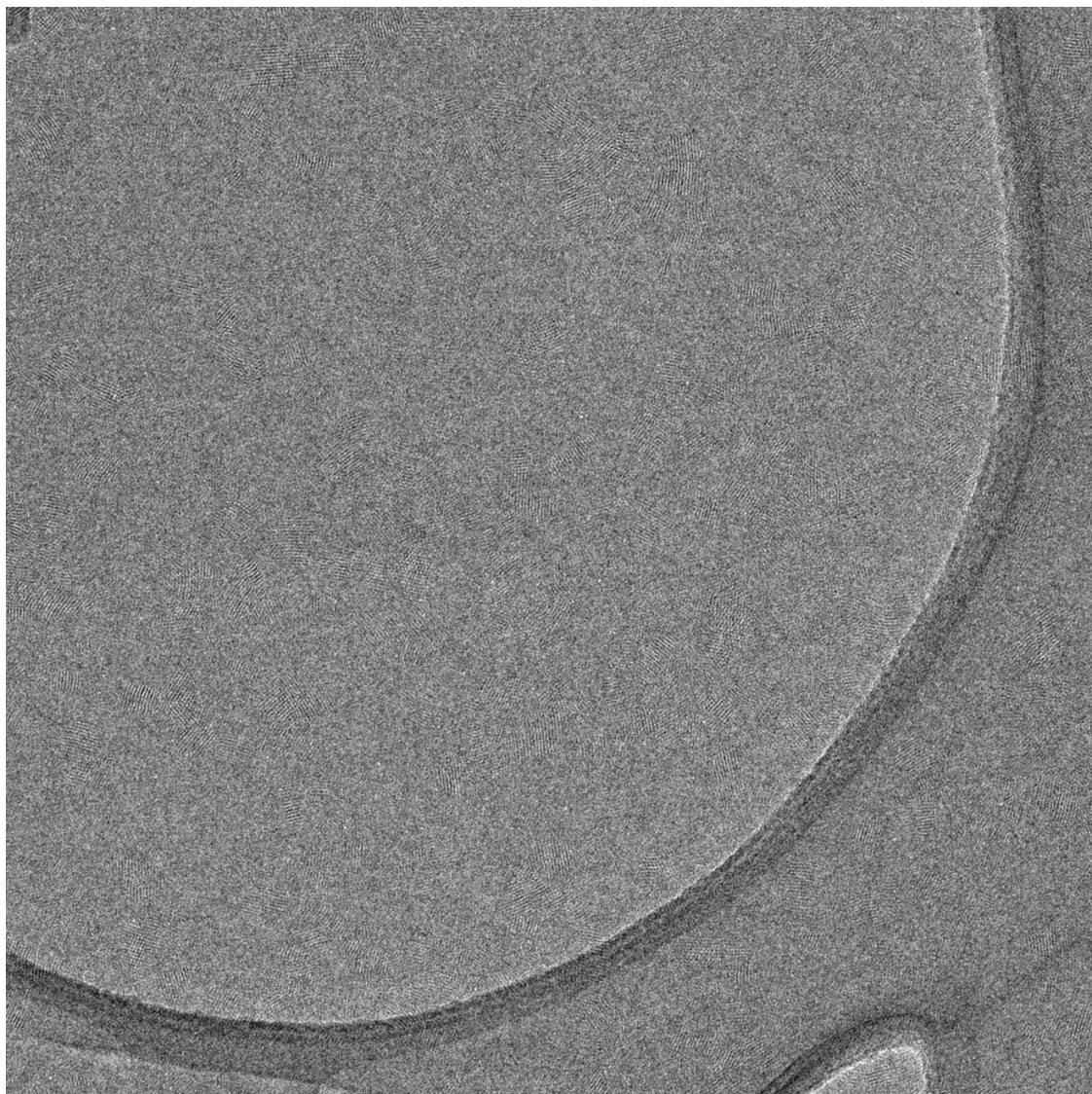


Figure S7. Larger image of impure *p*-DTS(PTTh₂)₂:PC₇₀BM blend films cast with 0.25% v/v DIO. Image is 650 nm on a side.

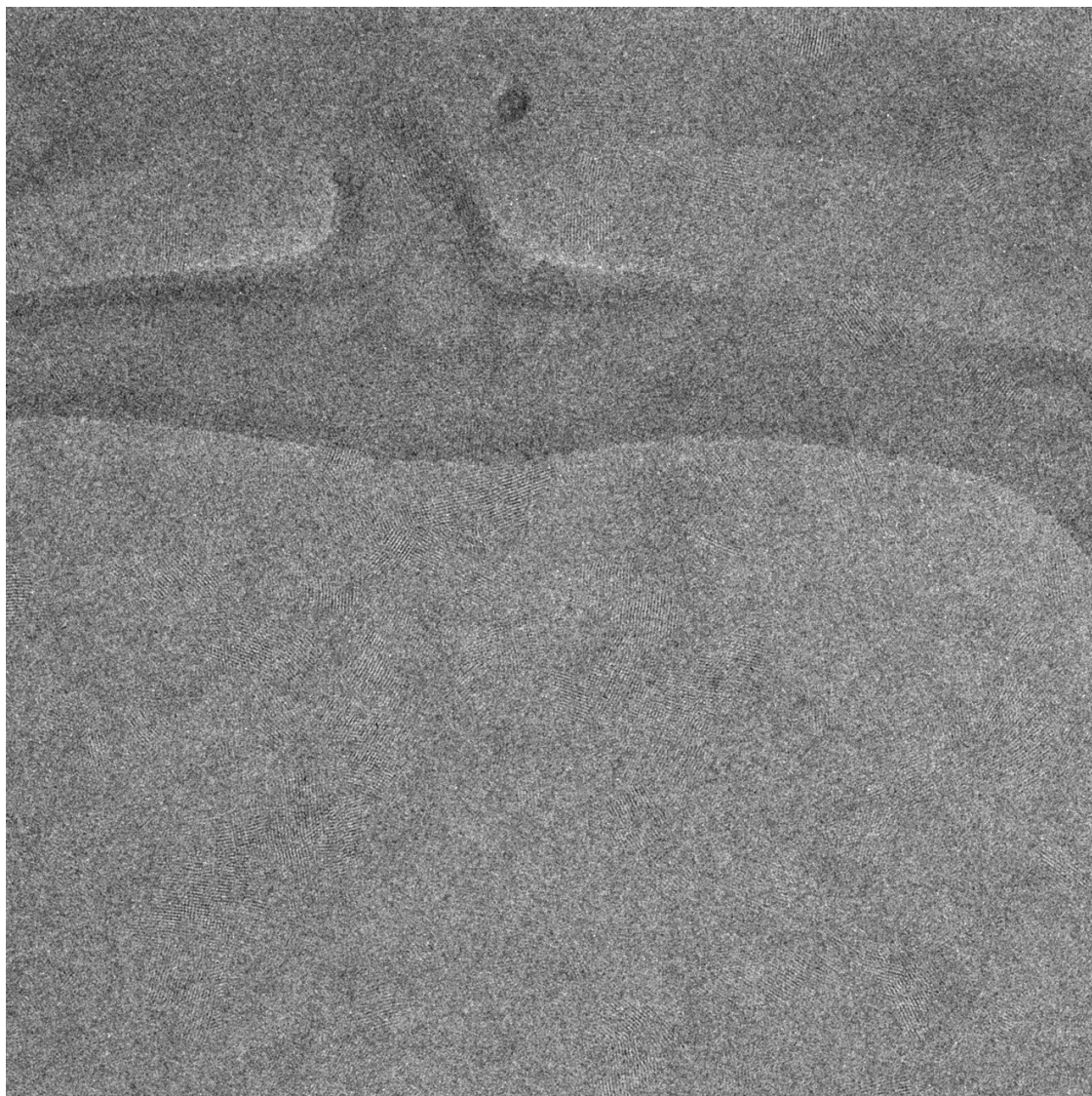


Figure S8. Larger image of pure *p*-DTS(PTTh₂)₂:PC₇₀BM blend films cast with 0.60% v/v DIO. Image is 650 nm on a side.

Reference:

- (1) Y. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan, A. J. Heeger, *Nat. Mat.* 2012, **11**, 44.