Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for Multi-step Ligand Exchange On P-type Quantum Dots Facilitates High-performance Solar Cells

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FMT ^{1}H NMR

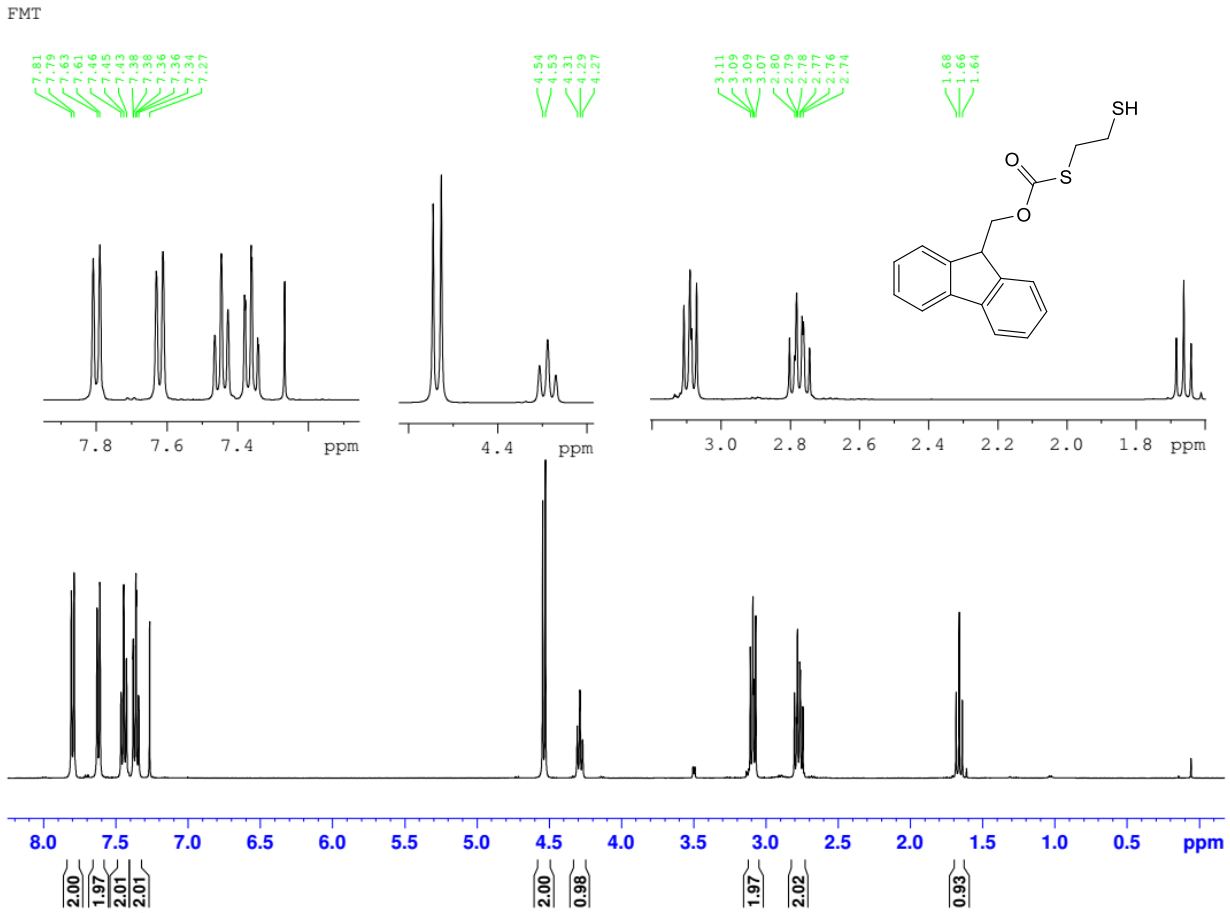


Figure S1: ^{1}H NMR of Pure FMT.

FMT ^{13}C NMR

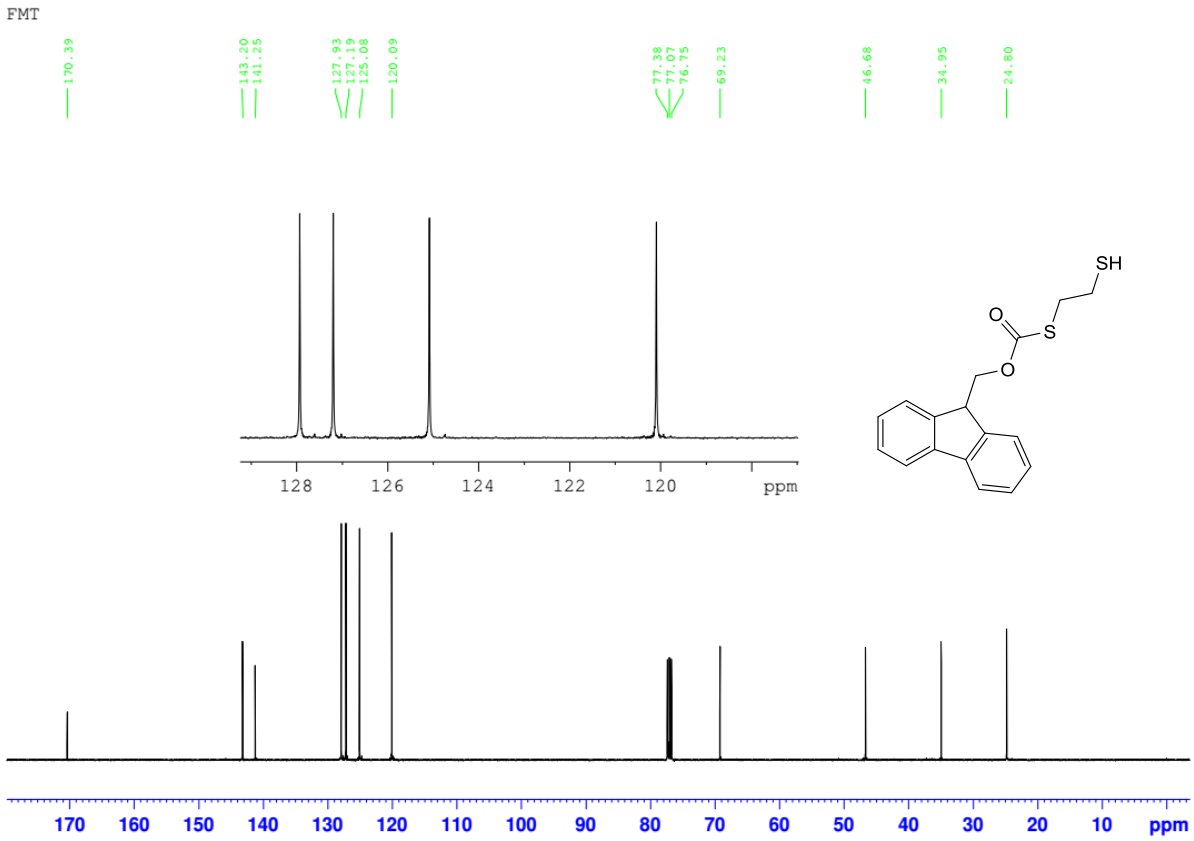


Figure S2: ^{13}C NMR for pure FMT.

^{1}H NMR of OA-PbS

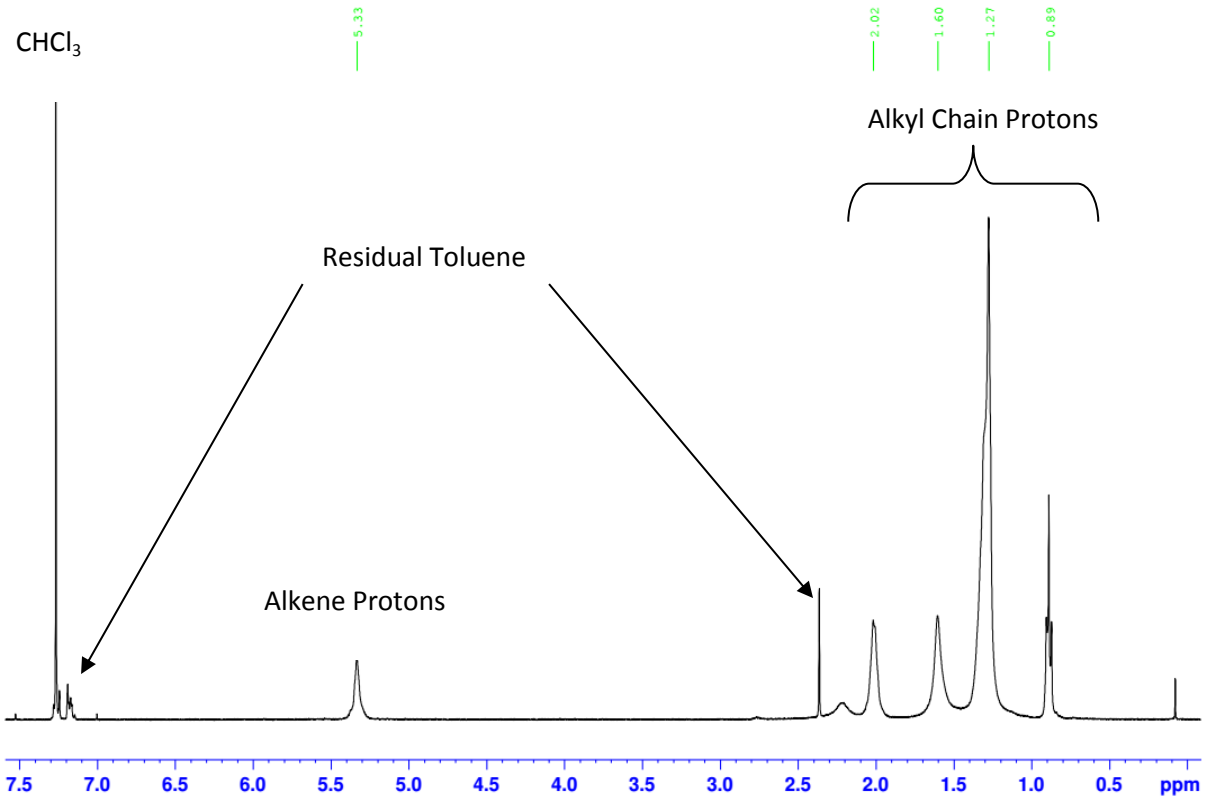


Figure S3: ^{1}H NMR of OA-PbS. Pertinent signals are marked.

^{1}H NMR of FMT-PbS

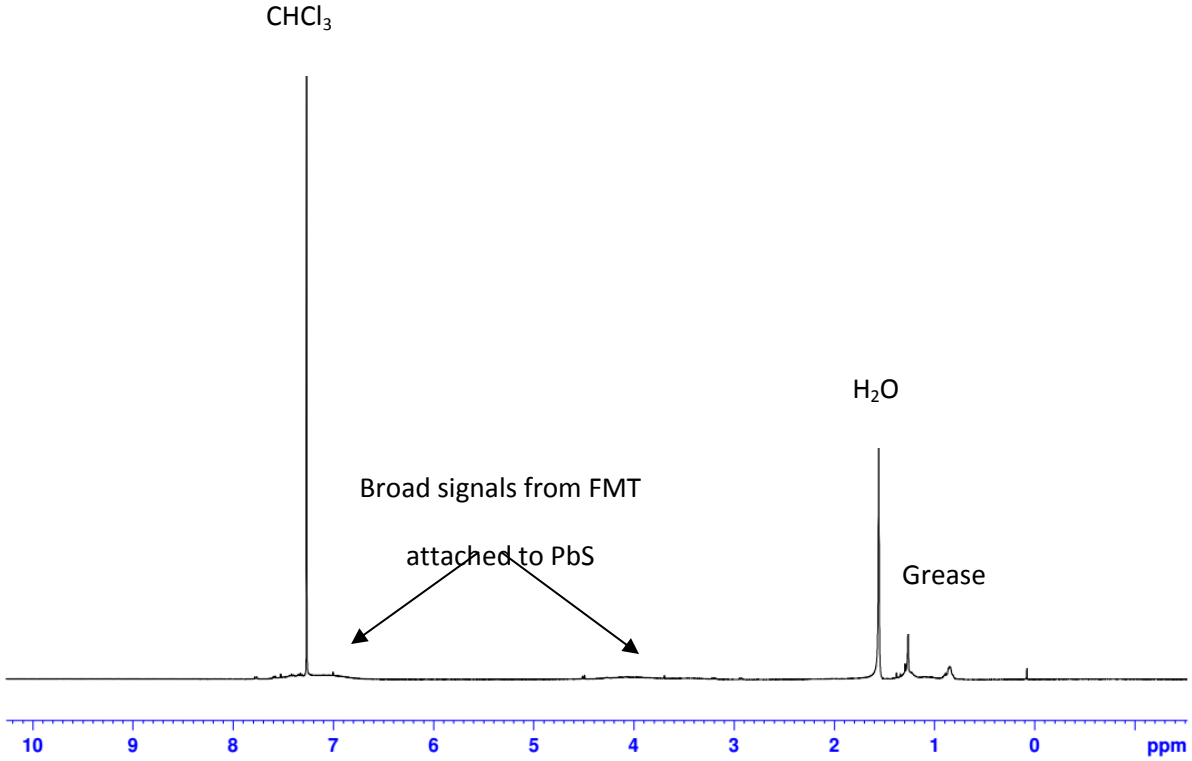


Figure S4: ^{1}H NMR of FMT-PbS. Pertinent peaks are marked.

XPS data

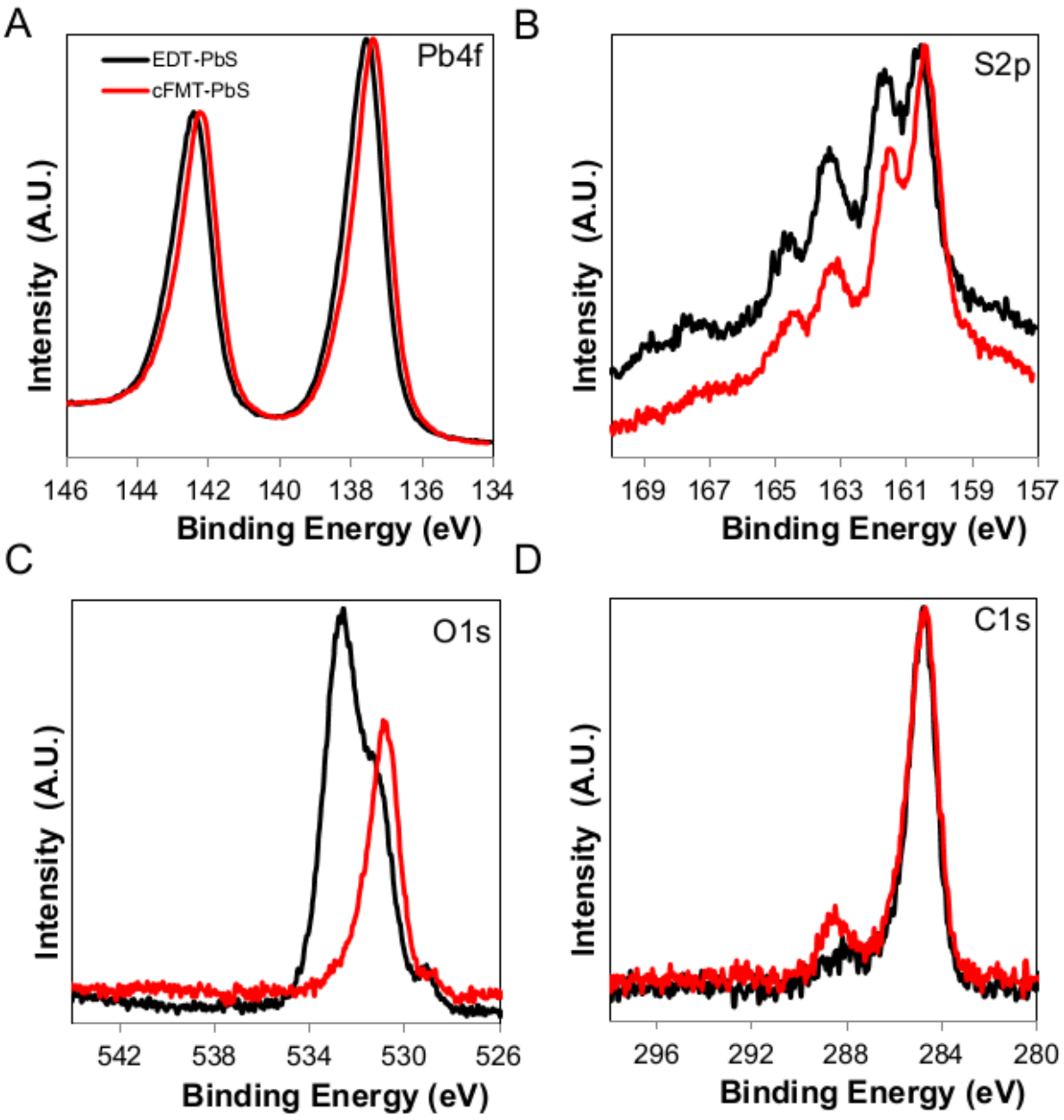
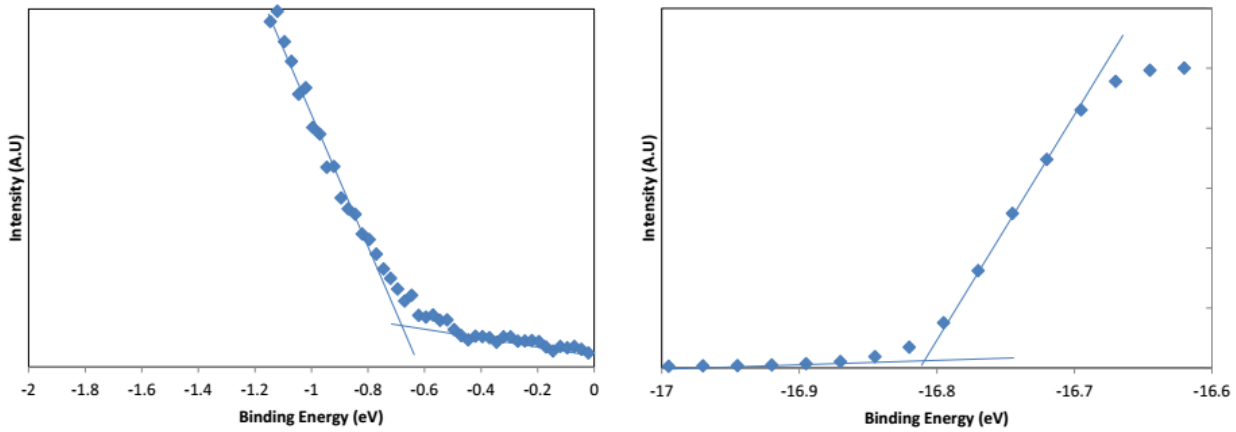


Figure S5: XPS spectra comparing a FMT- cleaved Film to an direct soak EDT-PbS Film. XPS spectra are shown for a) Pb 4f, b) S 2p, c)O 1s, d) C 1s. The C1s spectra for FMT contains a small signal at 289 eV which is likely due to residual ethyl acetate from the cleavage procedure.

UPS-EDT-PbS



UPS-cFMT-PbS

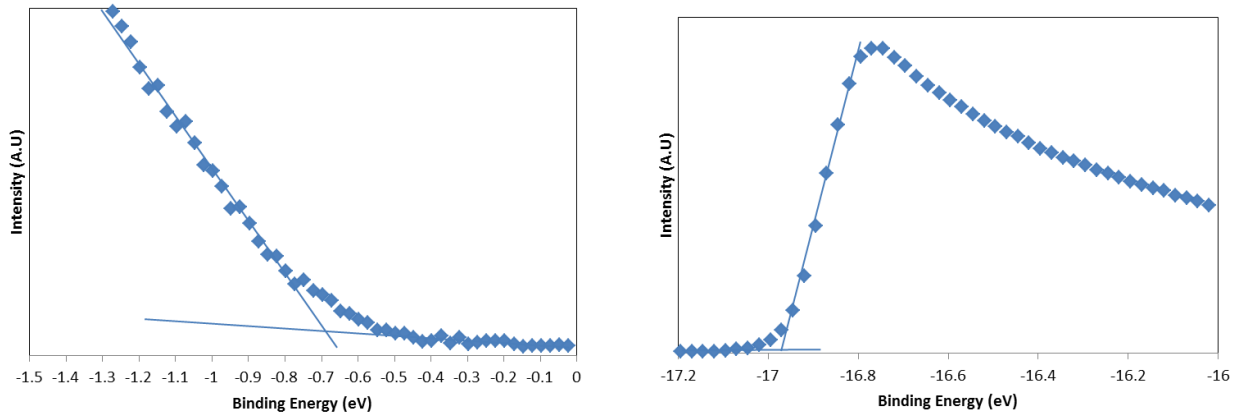


Figure S6: Ultraviolet Photoelectron Spectra comparing a directly soaked EDT film and a FMT-Cleaved EDT-PbS Film. A) Zoom in spectra of the high binding energies for a directly soaked EDT film. B) Zoom in spectra of the low binding energies for a directly soaked EDT film. C) Zoom in spectra of the high binding energies for a FMT cleaved EDT-PbS Film. D) Zoom in Spectra of the low binding energies for a FMT cleaved EDT-PbS film.

The values for the energy levels are as follows:
EDT- PbS: CB: 3.7 EF: 4.41 VB: 5.08
cFMT-PbS: CB: 3.5 Ef: 4.27 VB: 4.94

JV Sweeps

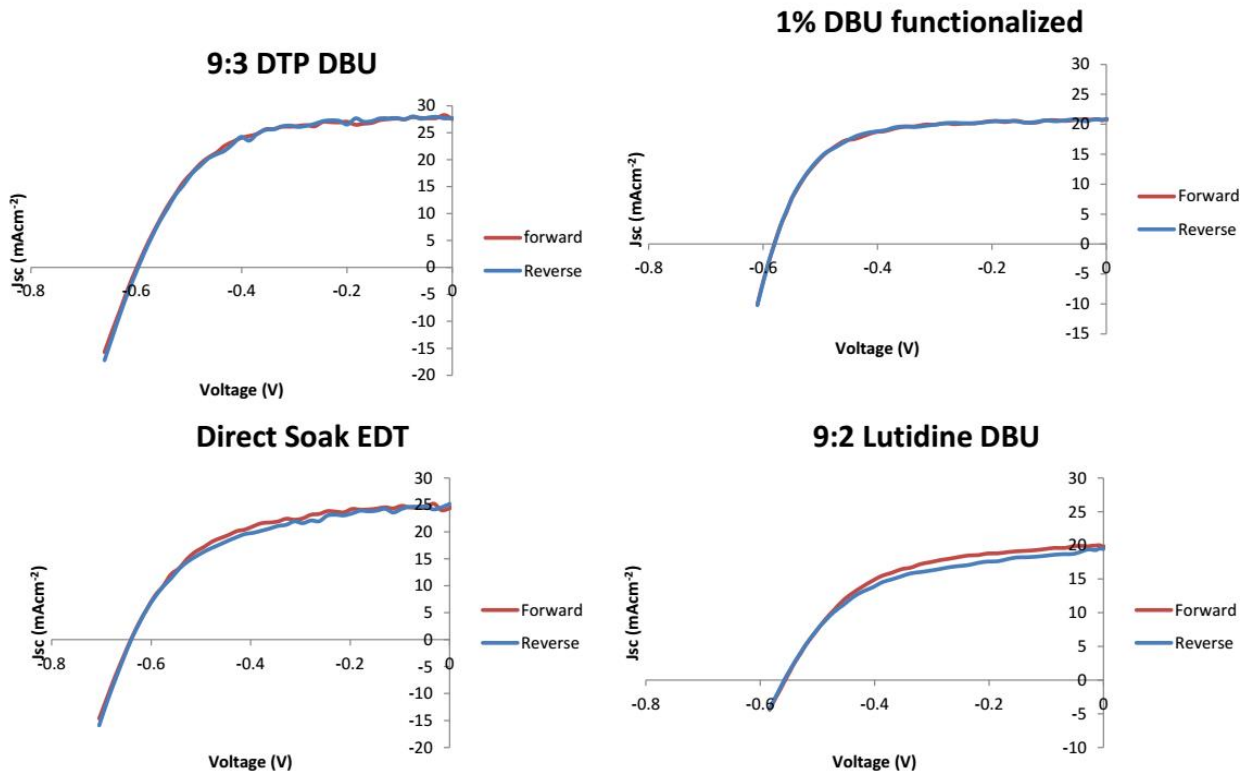


Figure S7: Full device characteristics for those tabulated in Table S5

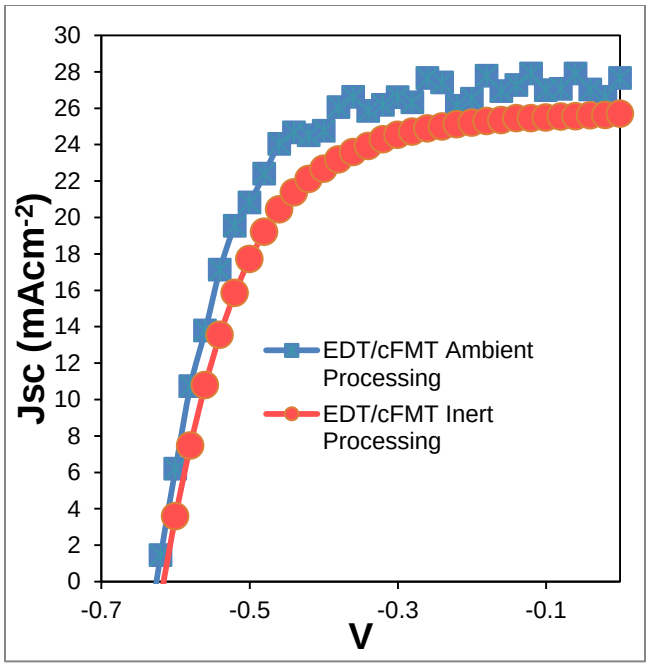


Figure S8: EDT/cFMT fabricated both in inert and ambient conditions.

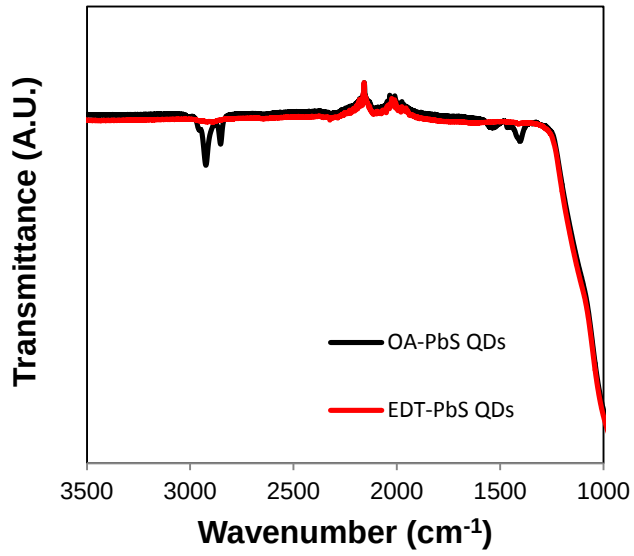


Figure S9: FTIR of EDT-PbS Films on glass substrates fabricated inside inert conditions. The disappearence of the –OH peak is seen.

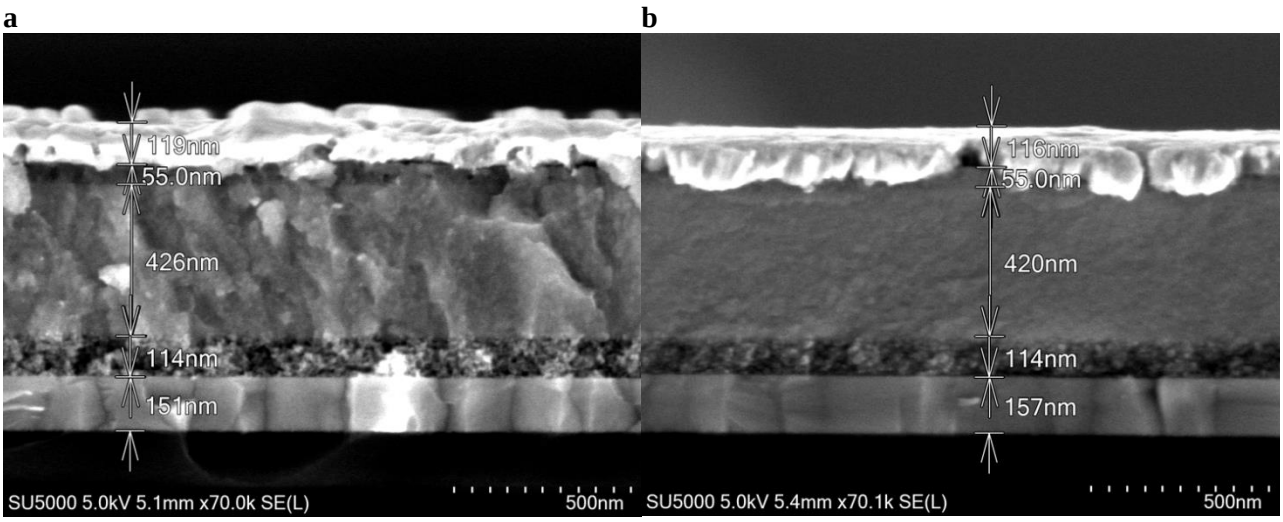


Figure S10: Cross sectional scanning electron microscope (SEM) images of both the EDT/EDT based device (a) and EDT/cFMT device (b) The layers are labelled as the following from top to bottom: Au, hole transport layer (HTL), PbS active layer, ZnO electron transport layer (ETL), indium doped tin oxide (ITO).

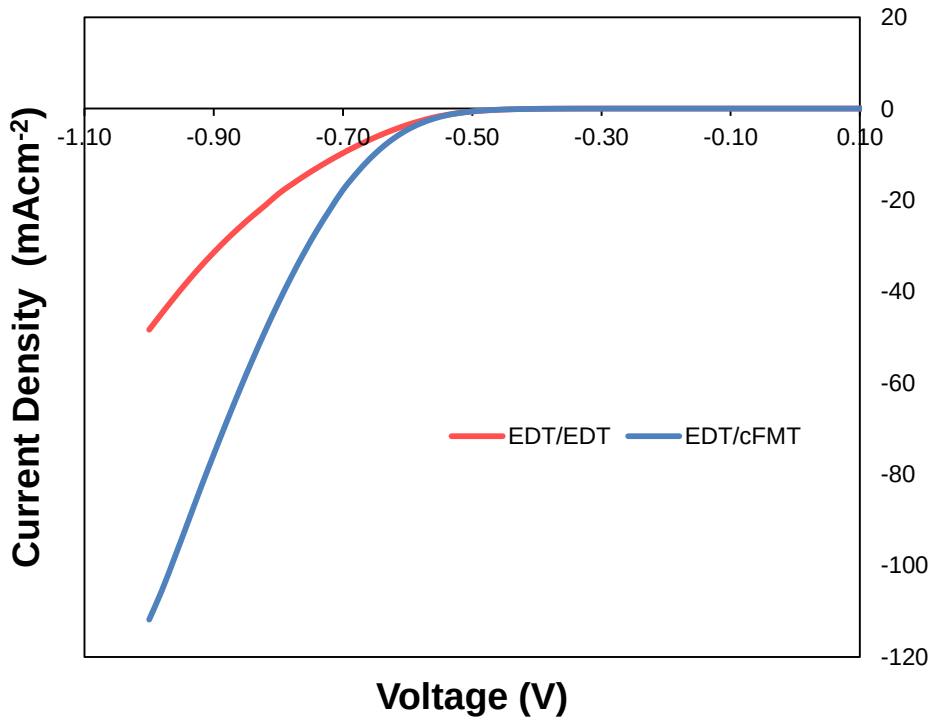


Figure S11: Dark J-V sweeps of an EDT/cFMT device and EDT/EDT device. JV sweeps were taken from devices aged after 18 days of storage in air. The R_{Series} of the EDT/cFMT device is 2.9 Ω cm^2 and the R_{Series} of the EDT/EDT device is 6.4 Ω cm^2.

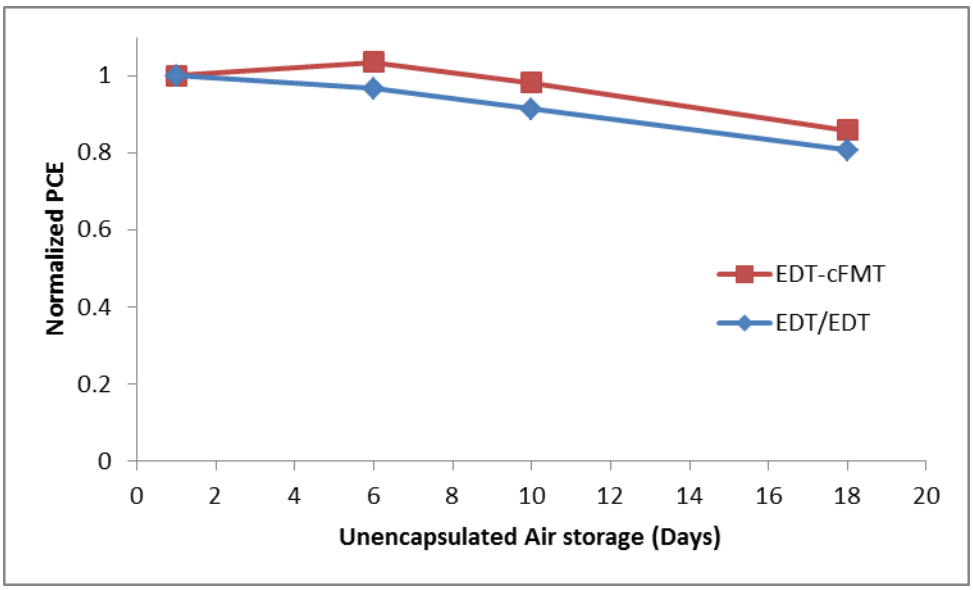


Figure S12: Stability tracking of an EDT/EDT device and a EDT/cFMT device.

Molecule	HOMO (eV)	LUMO(eV)	Bandgap (eV)
EDT	-6.73	-0.17	6.56
FMT	-6.22	-1.31	4.92

Table S1: HOMO, LUMO, and bandgap of EDT and FMT calculated from DFT.

Figure of Merit	Inert fabrication	Ambient Fabrication
Voc (V)	0.62±0.01	0.62±0.01
Jsc (mA cm^{-2})	24.39	25.68
FF (%)	42.8±1	59.4±1
PCE (%)	6.51	9.4

Table S2: Device figure of merit for an EDT/cFMT device fabricated in inert and ambient conditions.

	EDT/cFMT	
Day	1	18
Voc/V	0.63±0.01	0.61±0.01
Jsc/mA cm-2	28.44	27.20
FF/%	61±1%	56±1%
PCE/%	10.97	9.15

Table S3: Device figure of merit for stability of an EDT/cFMT device

	EDT/EDT	
Day	1	18
Voc/V	0.63±0.01	0.61±0.01
Jsc/mA cm-2	27.65	27.69
FF/%	64±1%	53±1%
PCE/%	11.05	8.88

Table S4: Device figure of merit for stability of an EDT/EDT device

Functionalization solvent	V_{oc} (V)	J_{sc} (mA/cm^2)	$FF_{forward}$ (%)	$FF_{reverse}$ (%)	PCE (%)
DBU only	0.58±0.01	20.77	66.02±1%	65.30±1%	7.80
9:2 v/v 2,6-lutidine: DBU	0.56±0.01	20.58	54.07±1%	51.17±1%	5.88
9:3 v/v DTP:DBU	0.60±0.01	26.96	59.72±1%	58.53±1%	9.56
EDT-PbS control	0.63±0.01	27.65	63.9±1%	63.4±1%	11.01
Graded: 1 Layer EDT-PbS + 1 layer 30:1 v/v DMPpy: DBU	0.66±0.01	27.41	60.65±1%	61.14±1%	11.01

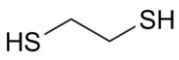
Table S5: Figure of Merit for Solar cells

	Normalized PCE	
Hours	EDT-EDT	EDT-cFMT
24±1	1	1
43±1	0.81	0.86

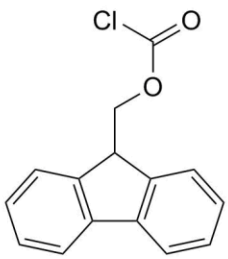
Table S6: Normalized PCE of EDT/EDT and EDT/cFMT devices stored over a period of 18 days.

Structures of Compounds Used

Reactants

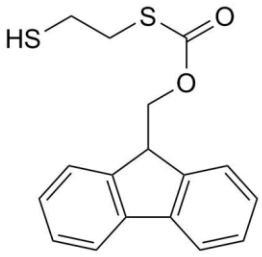


ethane-1,2-dithiol



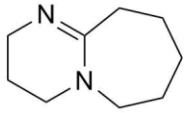
(9*H*-fluoren-9-yl)methyl carbonochloridate

Ligand

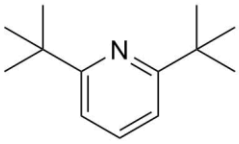


O-((9*H*-fluoren-9-yl)methyl) *S*-(2-mercaptoethyl) carbonothioate

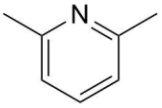
Bases



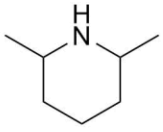
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)



2,6-ditert-butylpyridine



2,-6-lutidine (LUT)



2,6-dimethylpiperidine