

ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Photovoltaic Cells through Predictable Selection of Solvent
Additives

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Supporting Information

Solubility values were calculated using equations 1, 2, and 3 with group values taken from Barton¹ unless otherwise indicated.

$$\delta_D = (\sum_z {}^zF_D)/V \quad (1)$$

$$\delta_P = (\sum_z {}^zF_P^2)^{1/2}/V \quad (2)$$

$$\delta_H = (\sum_z {}^zU_H/V)^{1/2} \quad (3)$$

Where ${}^zF_D$, ${}^zF_P$, and ${}^zU_H$ are the molar group contributions for the dispersion, polar, and hydrogen bonding terms, and V is the total volume calculated from the sum of the individual groups.¹ It should be noted that due to the size of all molecules and the relatively large distance between polar groups, no corrections were made to δ_P to account for symmetry effects.

Table 1. Hansen solubility parameters as calculated for 1,8-diiodooctane.

Group	Occurrences	^zV (cm ³ mol ⁻¹)	^zF_D (J ^{1/2} cm ^{3/2} mol ⁻¹)	^zF_P (J ^{1/2} cm ^{3/2} mol ⁻¹)	^zU_H (J mol ⁻¹)	$\Sigma ^zV$ (cm ³ mol ⁻¹)	$\Sigma ^zF_D$ (J ^{1/2} cm ^{3/2} mol ⁻¹)	$\Sigma ^zF_P^2$ (kJ cm ³ mol ⁻²)	$\Sigma ^zU_H$ (J mol ⁻¹)
-CH2-	8	16.6	270	0	0	132.8	2160	0	0
>CH-	2	32.2	655	665	2046	64.4	1310	884	4092
Total						197.2	3470	884	4092

Applying equations 1, 2, and 3 results in $\delta_D = 17.6 \text{ MPa}^{1/2}$, $\delta_P = 4.8 \text{ MPa}^{1/2}$, and $\delta_H = 4.6 \text{ MPa}^{1/2}$.

Table 2. Hansen solubility parameters as calculated for TT-iI-TT.

Group	Occurrences	^zV (cm ³ mol ⁻¹)	^zF_D (J ^{1/2} cm ^{3/2} mol ⁻¹)	^zF_P (J ^{1/2} cm ^{3/2} mol ⁻¹)	^zU_H (J mol ⁻¹)	$\Sigma ^zV$ (cm ³ mol ⁻¹)	$\Sigma ^zF_D$ (J ^{1/2} cm ^{3/2} mol ⁻¹)	$\Sigma ^zF_P^2$ (kJ cm ³ mol ⁻²)	$\Sigma ^zU_H$ (J mol ⁻¹)
-CH3	6	31.7	419	0	0	190.2	2514	0	0
-CH2-	20	16.6	270	0	0	332	5400	0	0
>CH-	2	-1	80	0	0	-2	160	0	0
=CH-	14	12.4	223	70	143	173.6	3122	68.6	2002
=C<	16	-5.7	45	70	143	-91.2	720	78.4	2288
S	4	8	454	362	221	32	1816	524	884
-CON<	2	13.2	301	1229	4772	26.4	602	3020	9544
Total						661	14334	3692	14718

Applying equations 1, 2, and 3 results in $\delta_D = 21.7 \text{ MPa}^{1/2}$, $\delta_P = 2.9 \text{ MPa}^{1/2}$, and $\delta_H = 4.7 \text{ MPa}^{1/2}$.

Table 3. Hansen solubility parameters as calculated for PC₆₁BM.

Group	Occurrences	^zV (cm ³ mol ⁻¹)	^zF_D (J ^{1/2} cm ^{3/2} mol ⁻¹)	^zF_P (J ^{1/2} cm ^{3/2} mol ⁻¹)	^zU_H (J mol ⁻¹)	$\Sigma ^zV$ (cm ³ mol ⁻¹)	$\Sigma ^zF_D$ (J ^{1/2} cm ^{3/2} mol ⁻¹)	$\Sigma ^zF_P^2$ (kJ cm ³ mol ⁻²)	$\Sigma ^zU_H$ (J mol ⁻¹)
-CH3	1	31.7	419	0	0	31.7	419	0	0
-CH2-	3	16.6	270	0	0	49.8	810	0	0
=CH-	5	12.4	223	70	143	62	1115	24.5	715
=C<	1	-5.7	45	70	143	-5.7	45	4.9	143
>C<	1	-19.2	-70	0	0	-19.2	-70	0	0
-COO-	1	8.2	667	511	2557	8.2	667	261	2557
C60 ^a	1	409.5	8067	1188	2985	409.5	8067	1410	2985
Total						536.3	11053	1700	6400

^a For C₆₀ the literature values for δ_D , δ_P , δ_H are 19.7, 2.9, and 2.7 MPa^{1/2} respectively. With a volume of 409.5, the molar group contributions ^zF_D , ^zF_P , and ^zU_H were calculated to be 8067 J^{1/2}cm^{3/2}mol⁻¹, 1188 J^{1/2}cm^{3/2}mol⁻¹, and 2985 J mol⁻¹ respectively.

Applying equations 1, 2, and 3 results in $\delta_D = 20.6 \text{ MPa}^{1/2}$, $\delta_P = 2.4 \text{ MPa}^{1/2}$, and $\delta_H = 3.5 \text{ MPa}^{1/2}$.

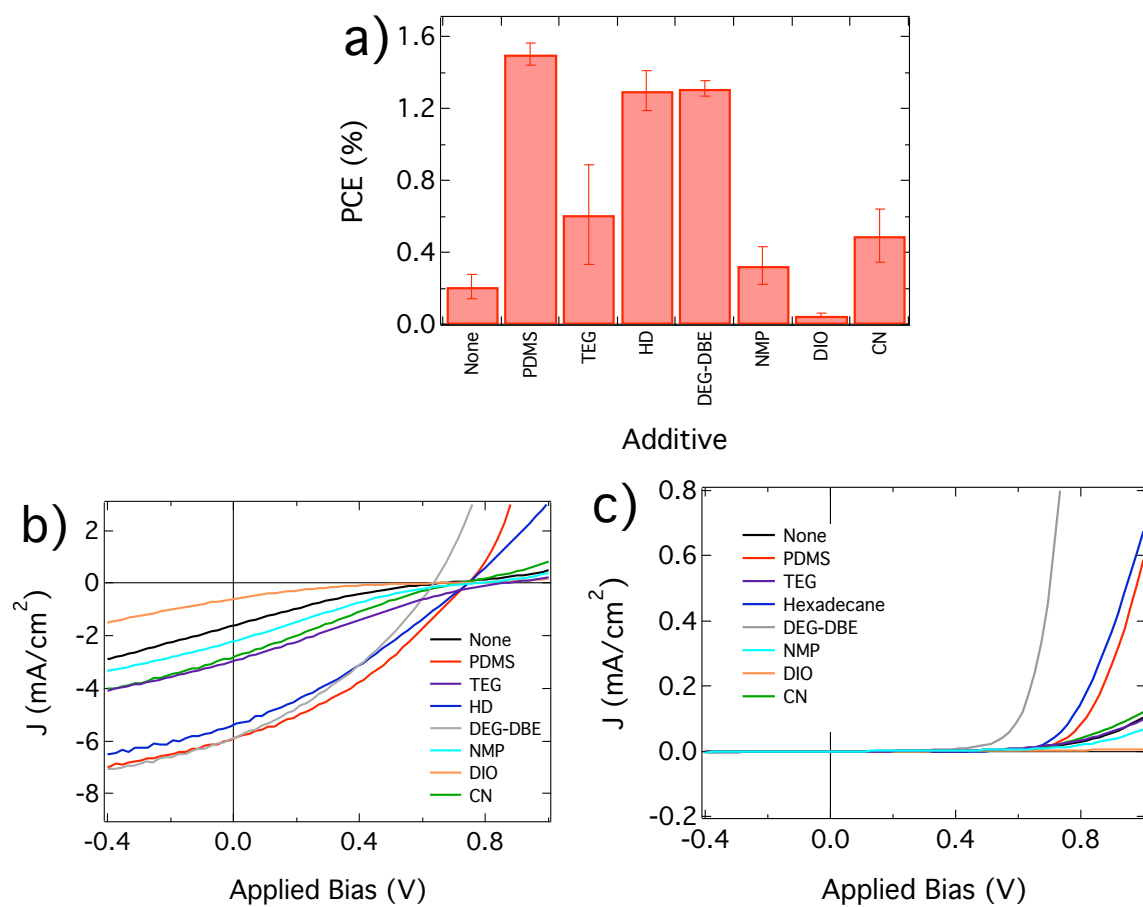


Figure 1. PCE of $\text{iI}(\text{TT})_2:\text{PC}_{61}\text{BM}$ devices with various additives with no thermal annealing (a) and current density vs. voltage characteristics for representative cells under AM1.5 illumination (b) and in the dark (c).

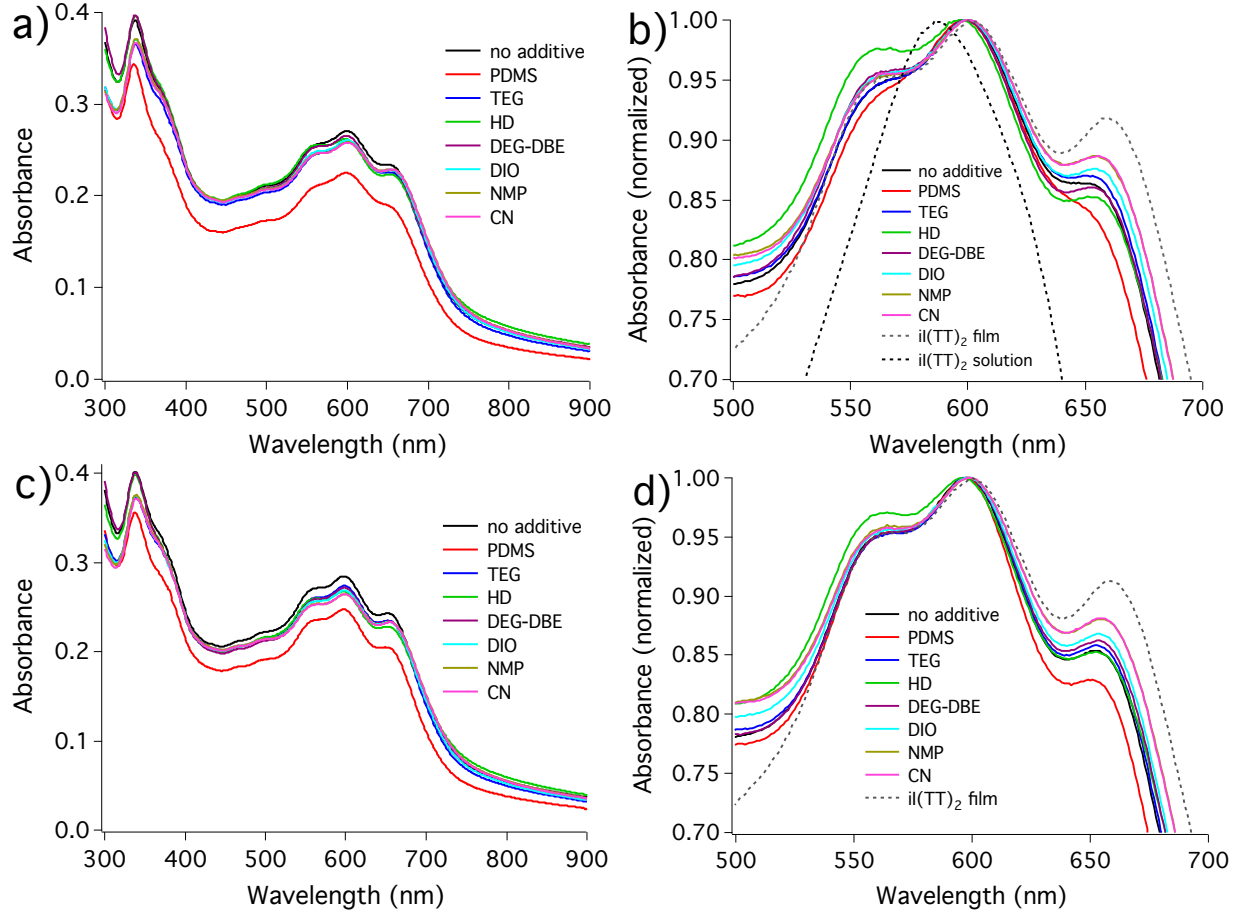


Figure 2. Absorbance of $iI(TT)_2:PC_{61}BM$ films with 1.0 mg/mL of various additives with no thermal annealing (a,b) and after thermal annealing at 100 °C for 20 minutes (c,d). Plots a and c show the full absorbance spectra before normalization whereas plots b and d show the normalized spectra in the $iI(TT)_2$ absorbance region. Plot b also contains the absorbance spectra of $iI(TT)_2$ in solution and plots b and d contain the spectra of $iI(TT)_2$ films without $PC_{61}BM$. Note the NMP and CN film absorbance spectra are nearly identical, thus making the NMP absorbance hard to see.

The field dependent SCLC model, equation 4, was used to extract the hole mobility in the SCLC devices.²⁻⁴

$$J = \frac{9}{8} \mu_0 \epsilon_r \epsilon_0 \exp(0.891 \gamma \sqrt{V/L}) \frac{V^2}{L^3} \quad (4)$$

Where a value of 3 was used for the relative permittivity, ϵ_r , and the thicknesses, L , of devices with additives was 75 nm while the device with no additive had a thickness of 85 nm. Igor pro was used to fit the data to equation 4 and extract the mobility, μ , and field dependent term, γ .

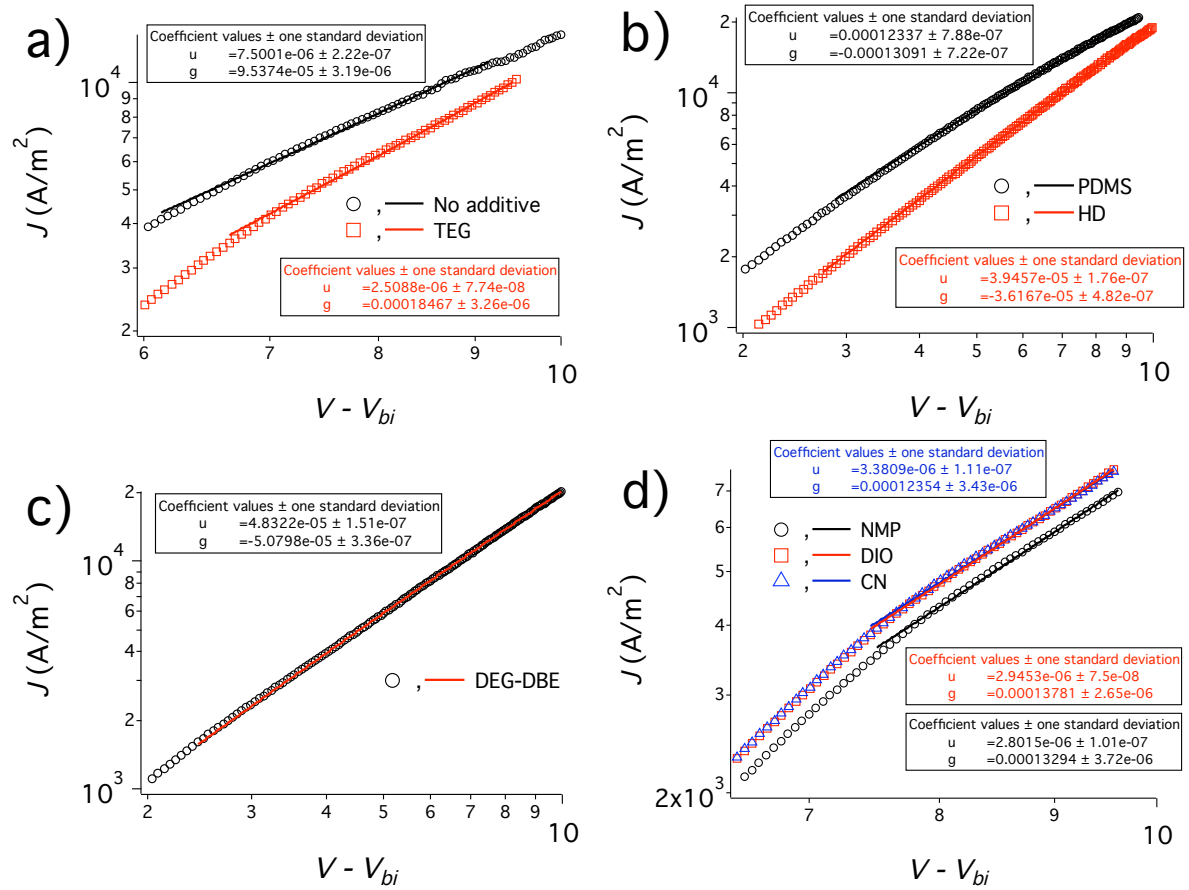


Figure 3. Current density vs. voltage plots with logarithmic scales showing the fit to the field dependent SCLC model for hole only devices with no additive and with TEG (a), with PDMS and HD (b), with DEG-DBE (c), and with NMP, DIO, and CN (d). The text boxes display the value of the hole mobility, μ (u), in $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and the field dependent term, γ (g), in $\text{m}^{1/2}\text{V}^{-1/2}$ measured for the individual pixels plotted with standard deviations of the fit to the data also shown.

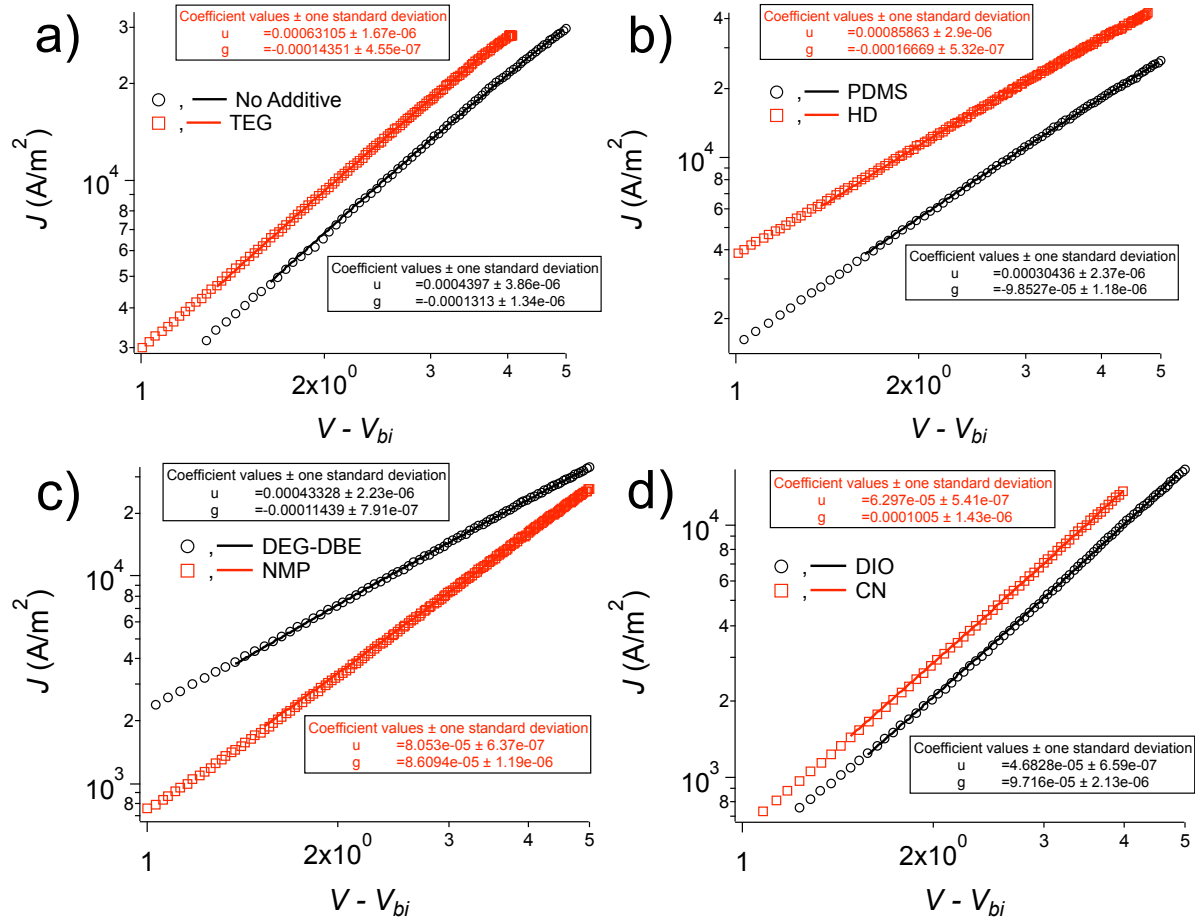


Figure 4. Current density vs. voltage plots with logarithmic scales showing the fit to the field dependent SCLC model for electron only devices with no additive and with TEG (a), with PDMS and HD (b), with DEG-DBE (c), and with NMP, DIO, and CN (d). The text boxes display the value of the electron mobility, μ (u), in cm²V⁻¹s⁻¹ and the field dependent term, γ (g), in m^{1/2}V^{-1/2} measured for the individual pixels plotted with standard deviations of the fit to the data also shown.

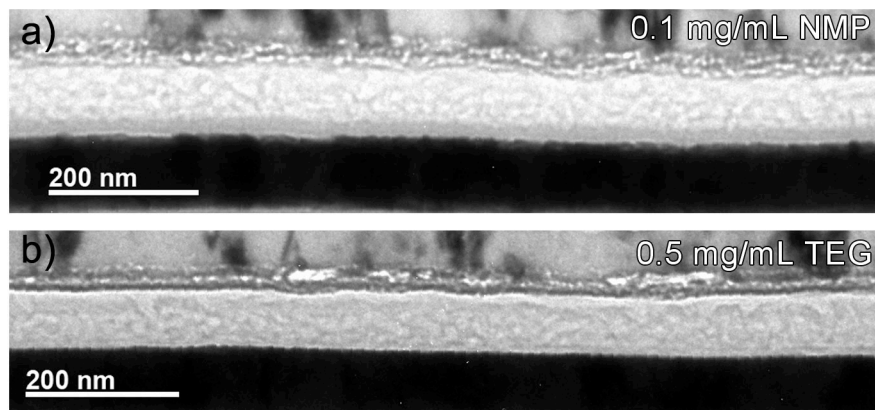


Figure 5. Cross sectional bright field TEM images of the devices with 0.1 mg/mL NMP (a) and 0.5 mg/mL TEG (b). It should be noted that the TEG sample was accidentally prepared from an area where the PEDOT:PSS had been wiped away, which is done in order to ensure direct contact to the ITO during device testing.

Table 4. Elemental composition of $iI(TT)_2$, $PC_{61}BM$, and PDMS with the number of atoms of each element per molecule shown along with the percent composition of that element relative to the total atoms present. Note that hydrogen is not included.

Material	# C (% C)	# N (% N)	# O (% O)	# S (% S)	# Si (% Si)
$iI(TT)_2$	60 (88.2)	2 (2.94)	2 (2.94)	4 (5.88)	0
$PC_{61}BM$	72 (97.3)	0	2 (2.7)	0	0
PDMS	2 (50)	0	1 (25)	0	1 (25)

From comparing the values from Table 4 with the elemental composition detected by XPS the relative percent of each material can be calculated. For example, since PDMS is the only material with Si and $iI(TT)_2$ is the only material with S the relative percent composition of each of these materials can be calculated based on equations 5 and 6.

$$\%PDMS = 100 \times \frac{\%Si}{25} \quad (5)$$

$$\%iI(TT)_2 = 100 \times \frac{\%S}{5.88} = 100 \times \frac{\%N}{2.94} \quad (6)$$

$$\%PC_{61}BM = 100 - \%PDMS - \%iI(TT)_2 = \frac{\%C - 88.2 \times \frac{\%iI(TT)_2}{100} - 50 \times \frac{\%PDMS}{100}}{97.3} \quad (7)$$

In general an average for % $iI(TT)_2$ and % $PC_{61}BM$ were calculated by using the two different equations listed in equations 6 and 7 respectively.

Table 5. Elemental composition as a function of the exit angle for the device containing 0.2 mg/mL 14,000 MW PDMS.

Exit Angle (°)	C (%) ^a	N (%) ^a	O (%) ^a	S (%) ^a	Si (%) ^a
15	59.9	0.8	22.4	2.3	14.6
45	76.8	1.6	11.9	4.1	5.6
90	80.2	2.3	8.2	4.8	4.5

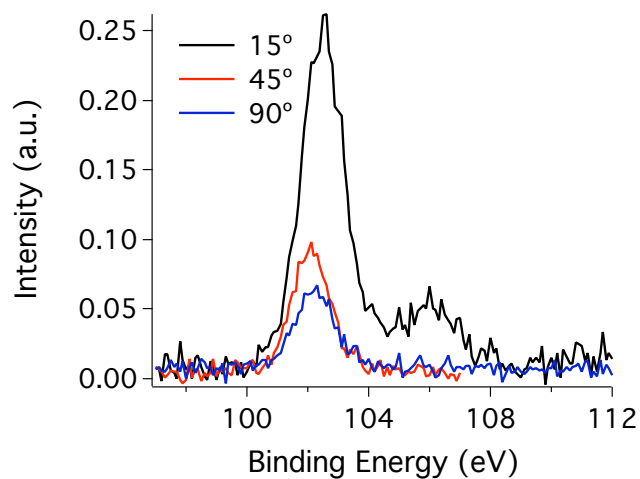


Figure 6. XPS data showing the 2p region of silicon for the device containing 0.2 mg/mL 14,000 MW PDMS at varying exit angles.

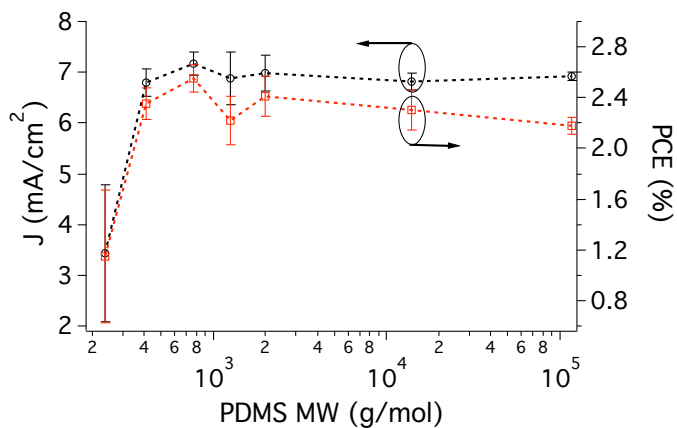


Figure 7. PCE and J_{SC} plots as a function of PDMS molecular weight (MW).

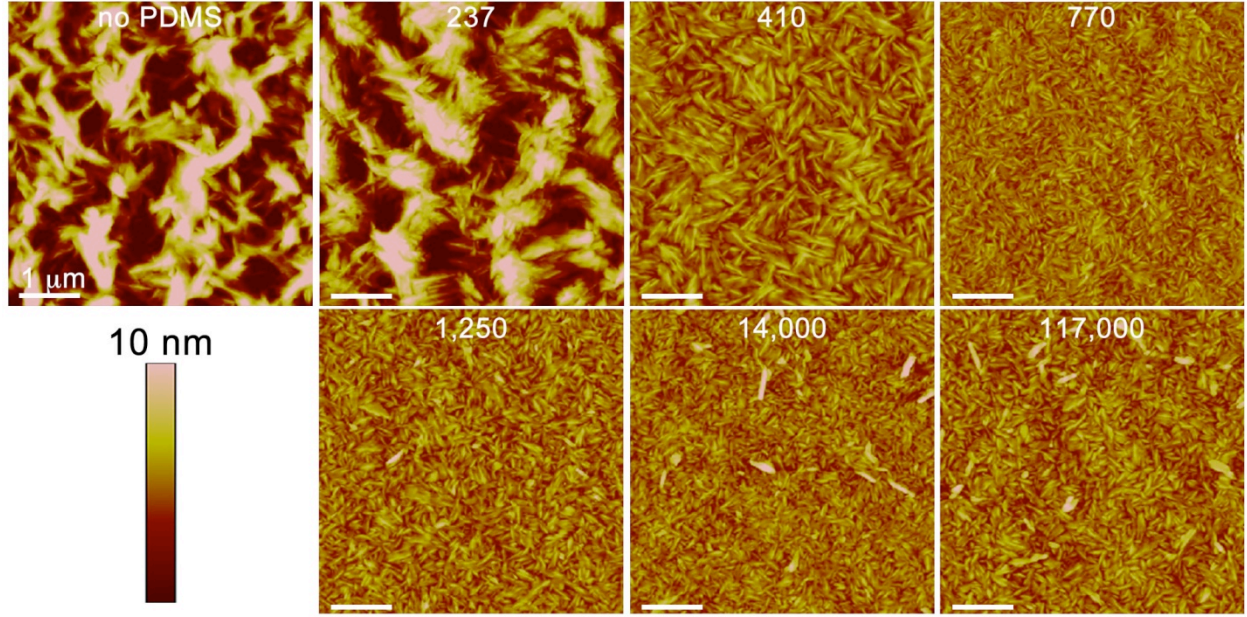


Figure 8. AFM height images of iI(TT)₂:PC₆₁BM blend films containing no PDMS and PDMS of varying MW after 100 °C thermal annealing for 20 minutes. All scale bars are 1 μm, number listed at top of images correspond to MW in g/mol.

Electroabsorption

The electroabsorption (EA) response is proportional to the imaginary part of the third order nonlinear dielectric susceptibility $\text{Im}\chi^{(3)}(h\nu)$ and the square of the electric field E .⁵

$$-\frac{\Delta T}{T} = \Delta\alpha d \propto \text{Im}\chi^{(3)}(h\nu) \times E^2 \quad (8)$$

Where α is the absorption coefficient and d is the film thickness. The electric field within the device is a combination of both the built-in field of the device along with the externally applied electric field:

$$E = E_{DC} - E_{bi} + E_{ac} \cos(\omega t) \quad (9)$$

Substituting Eq. (9) into Eq. (8), it is expected that the EA signal varies linearly with the applied DC bias and goes to zero when the applied DC bias is equal to the V_{BI} . Figure 8 shows the bias scans of the EA signal for devices illuminated with 702nm light which corresponds to the largest peak in the measured EA spectrum. When extrapolating the data, the zero-level crossing indicates their built-in potentials. As seen in Figure 8, the measured built-in potentials for the devices employing 0.2 mg/mL PDMS on PEDOT:PSS, 0.2 mg/mL PDMS and 0.5 mg/mL TEG on PEDOT:PSS, and 0.2 mg/mL PDMS on MoO₃ are 1.06V, 1.13V and 1.28V respectively.

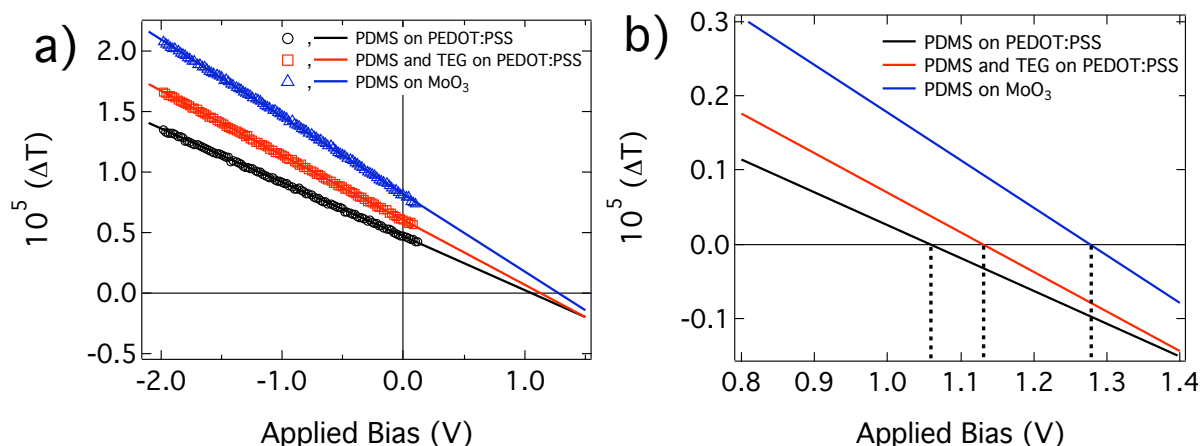


Figure 9. Bias dependence of the EA signal for devices with PDMS and/or TEG as additives on PEDOT:PSS or MoO₃ coated ITO substrates. Graph showing the whole range over which the fit was made (a) and a zoomed in view of where the fit crosses $\Delta T=0$.

Table 6. Summary of performance parameters for devices used for EA measurements, where LiF/Al was substituted for Ca/Al to enhance device stability.

Hole collecting layer	Additives (mg/mL)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
PEDOT:PSS	0.2 PDMS	0.78±0.02	7.2±0.4	0.37±0.02	2.1±0.2
PEDOT:PSS	0.2 PDMS and 0.5 TEG	0.95±0.01	7.7±0.2	0.39±0.01	2.9±0.1
MoO ₃	0.2 PDMS	0.96±0.01	8.0±0.1	0.45±0.02	3.4±0.1

Supporting Information Reference:

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