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Supplementary Information

Synergistic effect of carotenoid and silicone-based additives for photooxidatively stable organic solar cells with enhanced elasticity

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Concentration optimization of additives

Device	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
PTB7:[70]PCBM + PDMS				
PTB7:[70]PCBM	0.74±0.01	13.1±0.3	65.7±4.1	6.3±0.3
PTB7:[70]PCBM + 3 wt% PDMS	0.72±0.01	10.4±0.3	64.9±2.1	4.9±0.2
PTB7:[70]PCBM + 1.5 wt% PDMS	0.73±0.01	13.0±0.2	67.1±5.0	6.3±0.4
PTB7:[70]PCBM + 0.3 wt% PDMS	0.74±0.01	12.9±0.4	47.5±3.0	4.6±0.4
PTB7:[70]PCBM + 0.03 wt% PDMS	0.71±0.01	13.0±0.3	68.9±5.8	6.4±0.5
PTB7:[70]PCBM + AX				
PTB7:[70]PCBM	0.72±0.01	13.3±0.5	67.5±1.4	6.4±0.1
PTB7:[70]PCBM + 20 wt% AX	0.65±0.05	6.0±0.1	47.6±2.1	1.9±0.1
PTB7:[70]PCBM + 10 wt% AX	0.62±0.04	7.0±0.4	46.3±7.6	2.0±0.4
PTB7:[70]PCBM + 3 wt% AX	0.70±0.04	10.6±0.7	60.0±5.0	4.5±0.6
PTB7:[70]PCBM + 0.3 wt% AX	0.70±0.03	11.7±0.3	63.9±1.8	5.3±0.2
PTB7:[70]PCBM + 0.03 wt% AX	0.73±0.01	13.2±0.2	61.7±4.6	6.0±0.5

Supplementary 1. Photovoltaic parameters from the optimization process of the PTB7:[70]PCBM devices with and without the tested PDMS and AX additives. Standard deviation calculated on at least six devices.

Lifetime measurements

The long-term stability of the devices in Figure 3 is quantified using a bi-exponentially decaying function, with time constants t_1 and t_2 and corresponding initial PCE contributions A_1 and A_2, to characterize the initial fast and ensuing slow degradation components, respectively(1):

$$PCE(t) = y_0 + A_1 e^{-\frac{t}{t_1}} + A_2 e^{-\frac{t}{t_2}}$$

To evaluate the kinetics of the stabilizing effect of the tested additives, $t_{burn\text{-}in}$ and $t_{lifetime}$ were extracted from the bi-exponentially fitted curves.(2) The initial period of fast decay is referred to as $t_{burn\text{-}in}$, calculated analytically as(3):

Supplementary Information

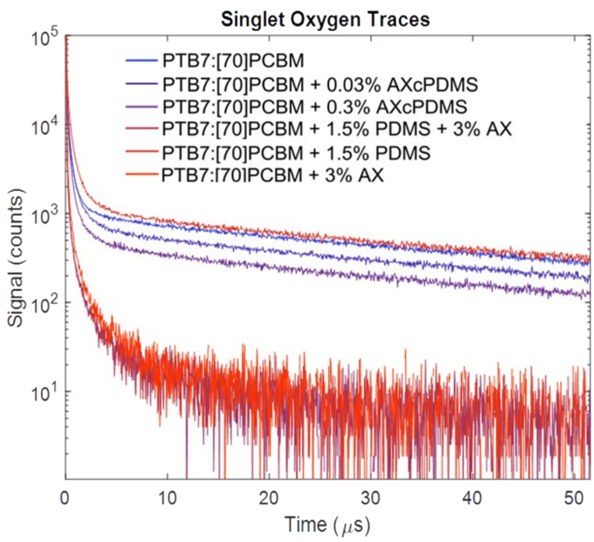
$$t_{burn-in} = \frac{t_1 t_2}{t_1 - t_2} ln\left(\frac{A_2 t_1}{A_1 t_2}\right)$$

The fast burn-in decay is followed by a slower degradation process, characterized by $t_{lifetime}$, which is defined as the time at which a further 20% reduction in performance has occurred with respect to the efficiency at the end of the burn-in period.

	PTB7:[70]PCBM	PTB7:[70]PCBM + 3 wt% AX	PTB7:[70]PCBM + 3 wt% AX + 1.5 wt% PDMS	PTB7:[70]PCBM + 0.3 wt% AXcPDMS	PTB7:[70]PCBM + 0.03 wt% AXcPDMS
y_0	**0,07 ± 0.00**	**0,05 ± 0,00**	**0,00 ± 0,00**	**0,26 ± 0,00**	**0,24 ± 0,01**
A_1	**7,06 ± 0,03**	**3,94 ± 0,04**	**4,08 ± 0,03**	**3,75 ± 0,05**	**4,86 ± 0,04**
t_1 (h)	**0,62 ± 0,01**	**0,98 ± 0,02**	**0,84 ± 0,01**	**1,10 ± 0,02**	**0,88 ± 0,01**
A_2	**1,39 ± 0,02**	**1,12 ± 0,02**	**0,99 ± 0,00**	**1,87 ± 0,02**	**1,66 ± 0,01**
t_2 (h)	**6,19 ± 0,07**	**12,27 ± 0,18**	**34,34 ± 0,40**	**12,68 ± 0,20**	**20,04 ± 0,30**

Supplementary 2. Fitting parameters and standard errors based on fit statistics for data presented in Table 2.

Singlet Oxygen Phosphorescence

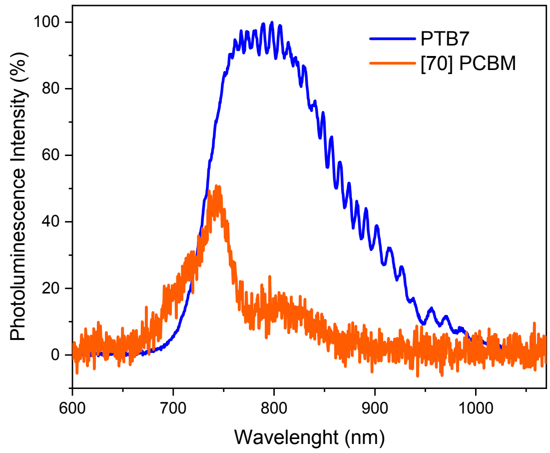


Supplementary 3. Time-resolved singlet oxygen phosphorescence signals recorded from PTB7:[70]PCBM films with different additives from Figure 4, zoomed in on the short timescales

PL measurements

The PL peak positions of PTB7:[70]PCBM blend films, and the pristine PTB7 and [70]PCBM films, are identified as the center position (x_0) of the Gaussian fits of the PL spectra.

Supplementary Information



Supplementary 4 Photoluminescence (PL) spectrum of pure PTB7 and [70]PCBM films.

PTB7

			Value	Standard Error	t-Value	Prob>|t|	Dependency
Photoluminescence Intensity	y0	Base	0.7201	0.15752	4.57145	5.13019E-6	0.34604
	xc	center	803.33819	0.3207	2504.97615	0	6.65501E-5
	A	area	14350.81146	83.76947	171.31314	0	0.56416
	w	FWHW	138.55017	0.81912	169.14551	0	0.43342

PCBM70

			Value	Standard Error	t-Value	Prob>|t|	Dependency
Photoluminescence Intensity	y0	Base	2.3259	0.10042	23.16257	1.06504E-105	0.17745
	xc	center	739.59727	0.45722	1617.61341	0	2.03938E-5
	A	area	2680.51761	38.51419	69.59819	0	0.45168
	w	FWHW	71.55324	1.11472	64.18952	0	0.3781

PTB7:PCBM70

			Value	Standard Error	t-Value	Prob>|t|	Dependency
Photoluminescence Intensity	y0	Base	44.36205	1.09594	40.47854	3.26089E-264	0.13587
	xc	center	740.29847	0.30593	2419.79266	0	1.19423E-5
	A	area	30014.72361	367.75766	81.6155	0	0.42394
	w	FWHW	54.77741	0.73907	74.11699	0	0.36656

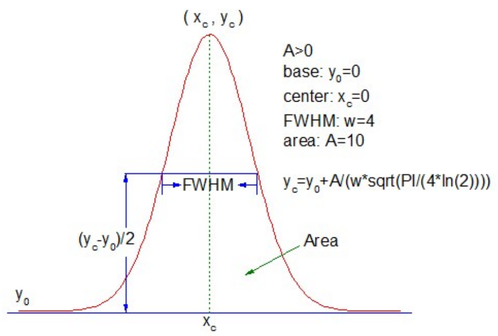
Supplementary Information

PTB7:PCBM70 + 3 wt% AX

			Value	Standard Error	t-Value	Prob>|t|	Dependency
Photoluminescence Intensity	y0	Base	52.74597	0.87032	60.60499	0	0.0908
	xc	center	743.53511	0.23036	3227.7406	0	5.28427E-6
	A	area	17724.86594	238.64748	74.27217	0	0.39388
	w	FWHW	36.59224	0.55141	66.36131	0	0.35482

PTB7:PCBM70 + 0.03 wt% AXcPDMS

			Value	Standard Error	t-Value	Prob>|t|	Dependency
Photoluminescence Intensity	y0	Base	39.67597	1.15226	34.43324	1.06756E-205	0.1332
	xc	center	740.42442	0.3165	2339.4495	0	1.1474E-5
	A	area	29653.17995	382.82703	77.45843	0	0.42216
	w	FWHW	53.69889	0.76415	70.27307	0	0.36584



Supplementary 5 Photoluminescence (PL) spectrum parameters of PTB7:[70]PCBM films for selected additive combinations

Solubility and Interaction parameters

Numerous reports have employed the Flory-Huggins interaction parameter (χ_{12}) to evaluate the miscibility between molecules in active layer blends.(4–6) The interaction parameter can be calculated as:

$$\chi_{12} = \frac{v_0}{RT}(\delta_1 - \delta_2)^2 \quad (1)$$

where v_0 is the lattice site volume, δ_1 and δ_2 are the Hildebrand solubility parameters of the two compounds, R is the ideal gas constant, and T temperature. The Hildebrand parameters were determined using Hansen solubility parameters (HSP) obtained from literature.

Supplementary Information

The site volume v_0 in equation (1) must be specified whenever discussing the interaction parameter as it is defined in terms of energy per site. When v_0 is fixed in equation (1), the value of $(\delta_1 - \delta_2)^2$ is proportional to the interaction parameter χ_{12} which is directly correlated to the miscibility of the two compounds.(4,7)

	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h(MPa$^{1/2}$)	δ_T (MPa$^{1/2}$)[e]	$(\delta_{T1}-\delta_{T2})^2$ (MPa)[f]
[70]PCBM[a]	19,8	4,0	4,6	20,7	-
PTB7[b]	21,1	2,2	5,9	22,0	-
PDMS[c]	14,9	0,4	0,8	14,9	-
AX[d]	18,3	4,0	4,4	19,2	-
[70]PCBM/PDMS	-	-	-	-	33,5
[70]PCBM/AX	-	-	-	-	2,2
[70]PCBM/PTB7	-	-	-	-	1,6
PTB7/PDMS	-	-	-	-	49,7
PTB7/AX	-	-	-	-	7,5
PDMS/AX	-	-	-	-	18,6

Supplementary 6 Hansen solubility parameters (δ_d, δ_p, δ_h), Hildebrandt solubility parameter (δ_T) of the donor, acceptor and additive molecules, and an estimate of the interaction parameters ($(\delta_{T1}-\delta_{T2})^2$) between them. a: values from (5)*; b: values from* (6)*; c: values from (8); d: values from HSPIP software; f: Hildebrandt solubility parameter calculated as* $\delta_T = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$ *; e: Interaction parameters estimated according to procedure in* (4)*.*

Mechanical testing

Blending brittle with ductile polymers can significantly improve the ductility of the organic devices made thereof.(9) The plasticizing polymeric additive is present in the active layers at very low loadings, thus the observed improved flexibility cannot be explained in terms of a simple weighed sum of the E_f of the active layer and the additive.(10)

We proposed that the observed improvement in flexibility of AX containing active layers, occurs due to a reduction in [70]PCBM aggregation in the presence of AX, which preferentially mixes with PCBM (see Supplementary 5) and also possibly forms hydrogen bonds with the PTB7 molecules.(11) The presence of PDMS in such blends interferes with the proposed mechanism, however when AX covalently bound to PDMS is added the beneficial effect can be reestablished.

Observing the cohesive fracture within the active layer (see Supplementary 6), the position of fracture will highly deviate from the reference active layers in the presence of PDMS alone, and PDMS blended with AX, where the fracture will occur at the interface to the bottom aluminum side, as well as in the presence of the higher loading of AXcPDMS, where the fracture will occur at the interface to the top glass side. We speculate that the reasons for this can be found in the presence of PDMS which does not mix well with the active layer

Supplementary Information

molecules but instead segregates on its edge, which then facilitates a fracture. At lower loadings of AXcPDMS the amount of PDMS is much lower, and as such allows better blending with the active layer molecules, thus resulting in a similar fracture position.

Cohesive fracture measurements

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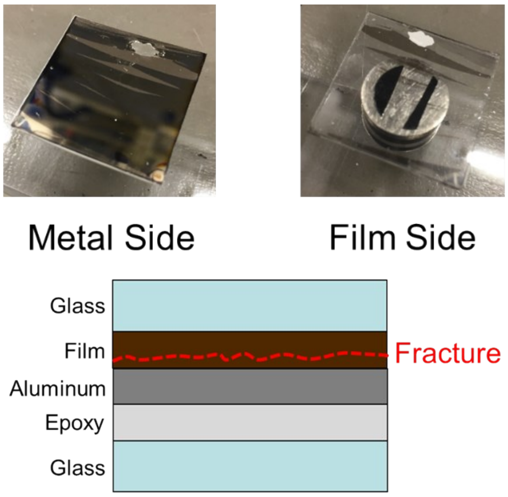
[70]PCBM</td>
<td>
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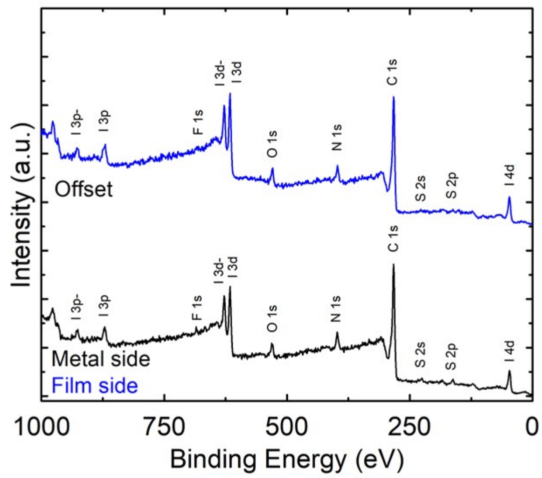
<td>
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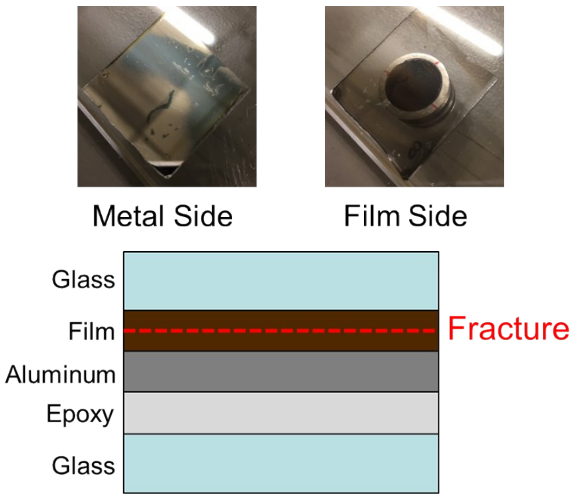
3 % AX</td>
<td>
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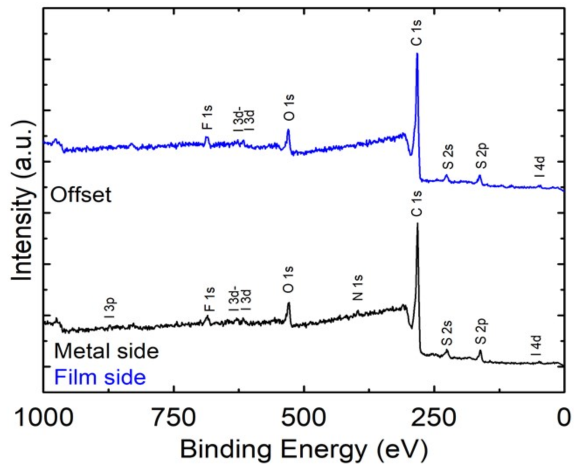
<td>
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Supplementary Information

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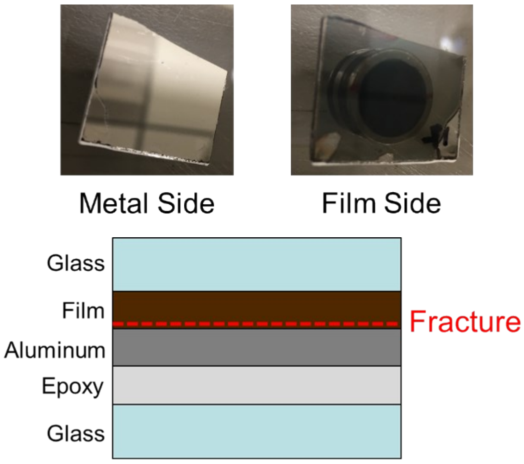
3 % AX +
1.5 %
PDMS10000</td>
<td>
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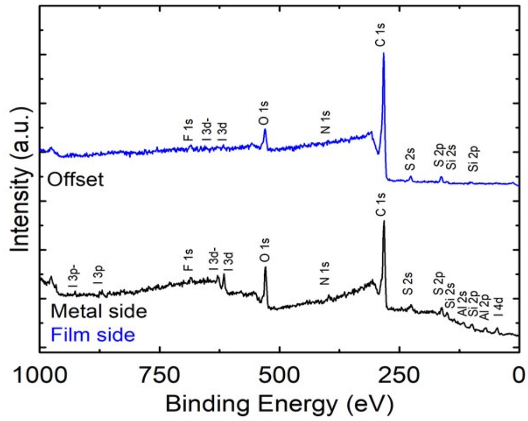
<td>
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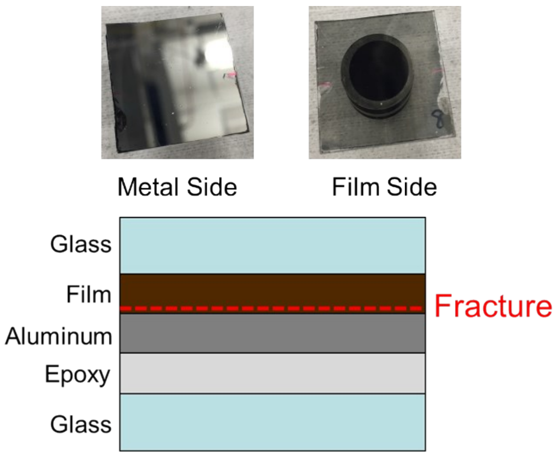
1.5 %
PDMS10000</td>
<td>
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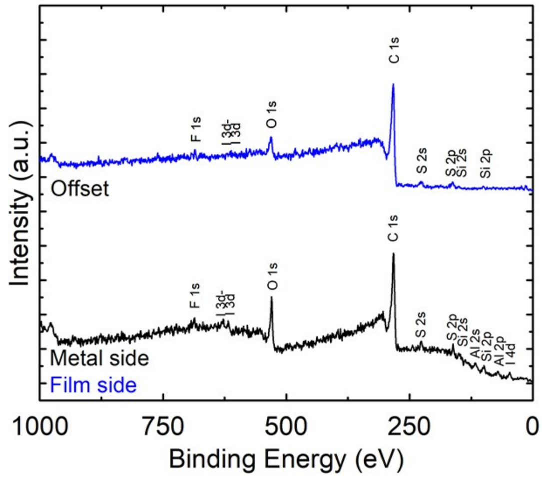
<td>
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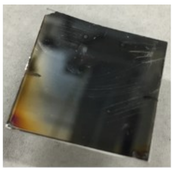
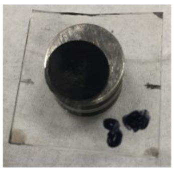
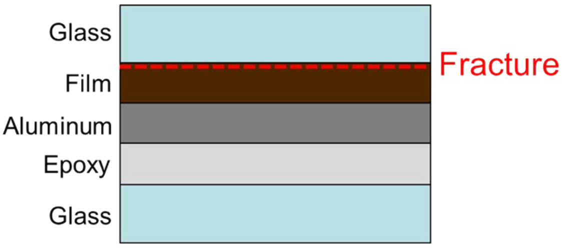
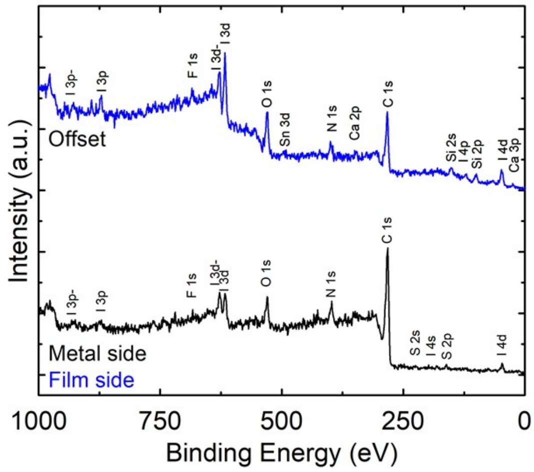
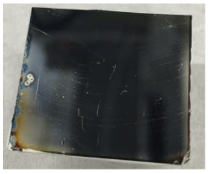
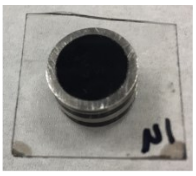
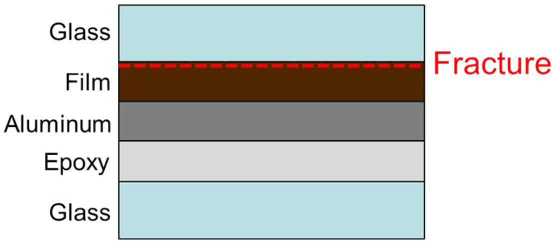
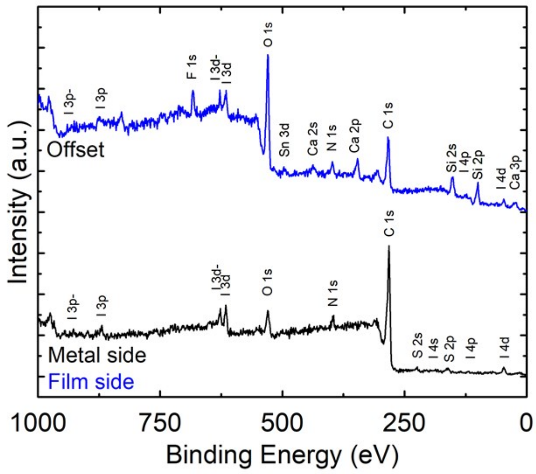
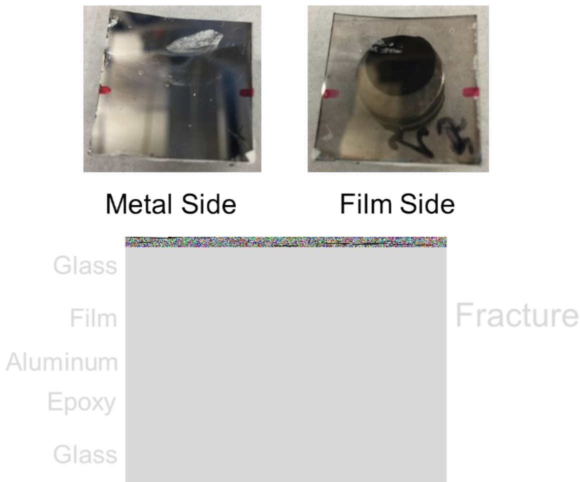
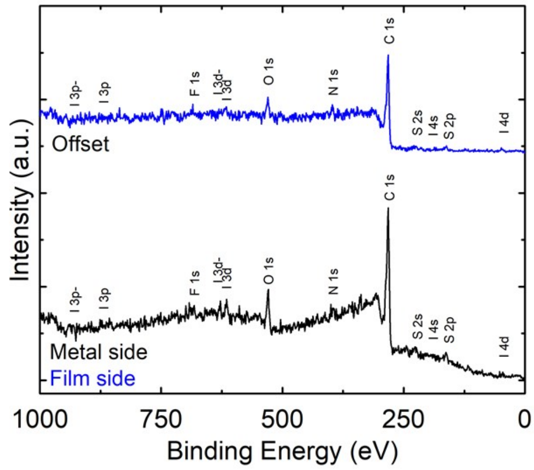
Supplementary Information

PTB7: [70]PCBM + 3 % AXcPDMS	 Metal Side  Film Side 	
PTB7: [70]PCBM + 0.3 % AXcPDMS	 Metal Side  Film Side 	

Supplementary Information

PTB7:
[70]PCBM +
0.03 %
AXcPDMS





Supplementary 7 X-ray Photoelectron Spectroscopy of the delaminated samples for both sides. Blue line indicating the film side and Black line indicating the metal side.

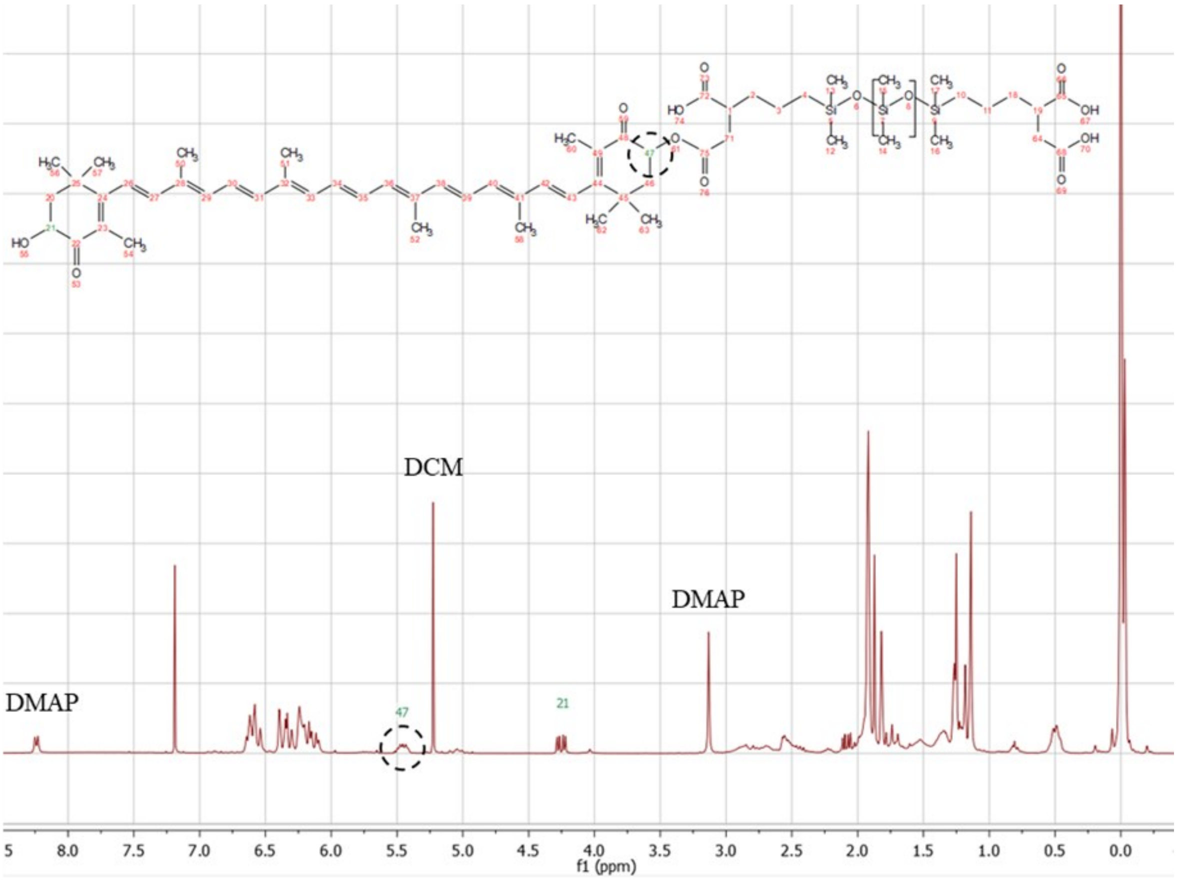
Elastic modulus

Thickness (nm)	PTB7:PCBM70		PTB7:PCBM70 +3%AX		PTB7:PCBM70 +1.5%PDMS		PTB7:PCBM70+3 %AX+1.5%PDMS		PTB7:PCBM7 0+0.3AXcPD MS		PTB7:PCBM70+ 0.03AXcPDMS	
rad/s	**Mean**	**Stdev**	**Mean**	**Stdev**	**Mean**	**Stdev**	**Mean**	**Stdev**	**Mean**	**Stdev**	**Mean**	**Stdev**
600	142.5	4.9	131.0	4.9	117.8	1.5	121.8	1.5	96.9	3.9	151.9	5.8
1000	116.3	5.0	99.2	4.1	97.4	5.0	95.8	3.9	66.9	1.6	113.2	3.6
3000	82.1	3.9	68.4	4.9	64.2	3.0	63.9	2.2	42.0	1.9	65.1	3.6

Supplementary 8. Thickness measurements of OPV films at different spin speeds (600 rad/s, 1000 rad/s and 3000 rad/s).

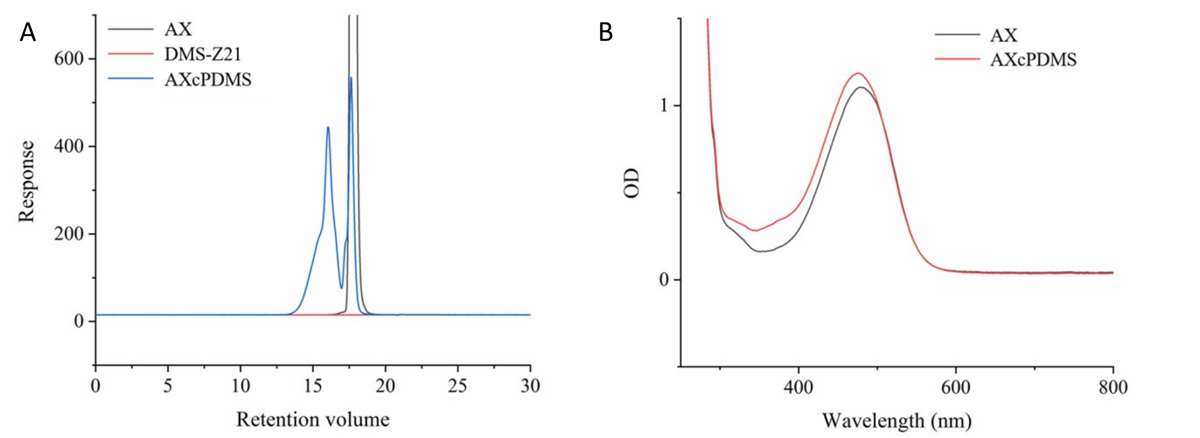
Supplementary Information

New additive molecule



Supplementary 9 1H NMR spectrum of the product AXcPDMS.

Supplementary Information



Supplementary 10 a) UV-vis detected GPC traces of free astaxanthin, DMS-Z21, and AXcPDMS (λ = 480 nm). b) UV-vis spectra of AXcPDMS and free astaxanthin. λ_{max} ASTA (in a mixture isopropanol/THF, due to the very poor solubility of ASTA in isopropanol) = 474 nm; λ_{max} PDMS/ASTA (in isopropanol) = 476 nm

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Supplementary Information

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