Supporting information

Spatial degradation mapping and componentwise degradation tracking in polymer-fullerene blends

Sample degradation

The samples were degraded under simulated sunlight and the spectrum used can be seen in figure S1. The samples were prepared based on degradation rates established previously, [1] and controlling the degradation time see table S2.

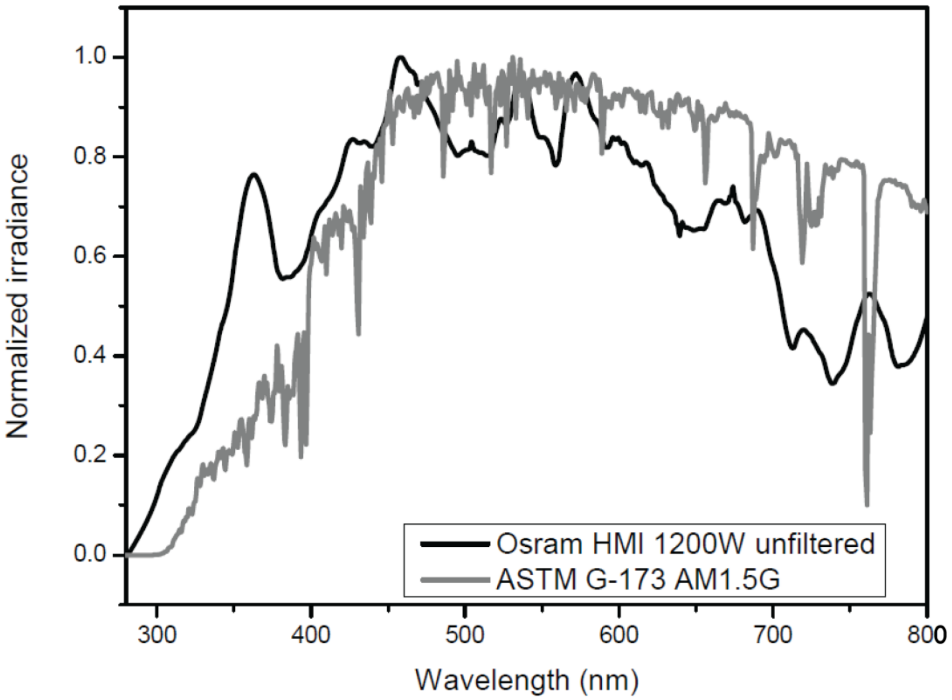

Figure S1: Irradiance of the 1200 W HMI lamp from Osram and the ASTM G-173 AM1.5 reference solar spectrum.

Material	Optical density	Degradation rate (%/h)	T80 (h)	T60 (h)	T40 (h)	T20 (h)
P3HT	0.47	2.5	8	16	-	34
PC60BM	1.0	0.36	60	120	-	-
P3HT-PC60BM	0.69	0.36	60	120	180	-

Table S2: The measured optical density, shown along with the previously established degradation rates. The degradation of samples was controlled through the exposure time, shown in the table in hours for the different samples.

Lambert-Beers law and linear combination of NEXAFS spectra

Through linear combination of the pure NEXAFS spectra of pure materials we have been able to match NEXAFS spectra of films consisting of blends.The linear combination of the spectra is expected from Lambert-Beers law for photon absorption. Assuming you have two materials A and B (without chemical interactions) the X-ray intensity after penetration, I, is given by the initial intensity, I_0, the thickness, x, and absorption coefficient, λ ,

$$I = I_0 \exp(-\lambda_a x_a) \exp(-\lambda_b x_b) . \quad \textbf{(1)}$$

The optical density of the blend material can be written as a linear combination of the pure optical densities, OD, by reformulating the thickness, x, into the new parameter, k,

$$OD_{ab} = \ln(I_0 / I) = k_a OD_a + k_b OD_b \quad \textbf{(2)}$$

Assuming the materials do not chemically interact during photo degradation, the optical density of the blend can be found as linear combination of the individual optical densities. The most likely individual degradation state of P3HT and $PC_{60}BM$ in a degraded P3HT-$PC_{60}BM$ sample can be found as the linear combination that fits the blend spectra best.

Reduced chi squares of Degraded P3HT-$PC_{60}BM$ blends

In the main text NEXAFS spectra are shown for degraded P3HT and $PC_{60}BM$ and P3HT-$PC_{60}BM$ blends along with componentwise degradtion. In table S2 we show the reduced chi-squares obtained when fitting all possible linear combinations to each blend. We did perform more meassurements of each blend state, but only T60 showned different NEXAFS spectra.
(The notation: T100 is pristine material and T80 indicate 80% of the pristine photo absorbance is left in the wave length interval 400 – 600 nm.)

Blend T100	PC60BM T60	PC60BM T80	PC60BM T100
P3HT T20	1.0	1.1	0.81
P3HT T60	0.86	0.86	**0.63**
P3HT T80	0.91	0.86	**0.58**
P3HT T100	0.89	0.88	**0.58**

BLEND T80	PC60BM T60	PC60BM T80	PC60BM T100
P3HT T20	1.5	1.4	1.1
P3HT T60	0.87	0.72	**0.40**
P3HT T80	1.2	0.79	**0.41**
P3HT T100	1.1	0.84	**0.37**

BLEND T60a	PC60BM T60	PC60BM T80	PC60BM T100
P3HT T20	2.0	0.73	1.4
P3HT T60	1.1	**0.10**	0.77
P3HT T80	1.8	**0.16**	0.98
P3HT T100	1.3	**0.098**	0.59

BLEND T60b	PC60BM T60	PC60BM T80	PC60BM T100
P3HT T20	**0.048**	0.59	0.74
P3HT T60	**0.048**	0.64	0.87
P3HT T80	**0.048**	0.53	0.74
P3HT T100	**0.048**	0.63	0.86

BLEND T40	PC60BM T60	PC60BM T80	PC60BM T100
P3HT T20	**2.3**	5.1	5.4
P3HT T60	**2.3**	5.4	5.8
P3HT T80	**2.3**	4.9	5.3
P3HT T100	**2.3**	5.3	5.8

Table S3: The individual degradation steps of P3HT-$PC_{60}BM$ blends are assigned by least reduced chi squares in linear combination of degraded P3HT and $PC_{60}BM$. The chi square of each linear combination is shown for each blend sample and the most likely degradation steps have been marked.

NEXAFS spectra for the various fullerenes and P3HT-fullerene blends – an estimator of robustness

This section deals with a small side study used to investigate our data treatment method and works as a proof of principle which we use to validate the method and estimate its robustness. For this purpose we use P3HT, different fullerenes and P3HT-fullerene blends spectra (shown in supporting information)**.**

We measure the NEXAFS spectra of pure P3HT and various fullerenes to be used as in the reference spectra. As 'unknown' test spectra we use the P3HT-fullerene blends and study how well our method assigns the correct material blend when using all linear combinations of P3HT and the fullerenes as reference spectra. The resulting fit and chi-squares can be seen in figure S4 and table S5**.** Due to uncertainty in the experiments (all spectra are obtained through measurements) we would expect some uncertainty in our method. We set a threshold of 0.1, meaning that if any chi-square is within 0.1 of the lowest chi-score they are also likely linear combinations. With the chosen threshold, our proof of principle gives reasonable results, which indicate it is an accurate measure for the robustness of the method.

For 3 of the blends (PC$_{70}$BM, C60, bisPCBM) the fullerene component is determined correctly and unambiguously. Two fullerenes (PC$_{60}$BM and ICBA) are determined correctly but with ambiguity e.g. for P3HT-PC$_{60}$BM both PC$_{60}$BM and C60 are selected as likely components. For P3HT-C70 our method instead predict PC70BM as the most likely component. The problem here lies with the recorded "C70 spectrum", which appear to be missing two prominent peaks as indicated in figure S4. We suspect the "C70 spectrum" is actually a measurement of unknown contamination and therefore not accurate, or representative of our methods performance.

Overall, the results support our method of component assignment in blends, and show the limitation i.e. ambiguity between components with similar spectra. With this limitation in mind the method does offer a feasible way to determine the components and the componentwise degradation in blend materials.

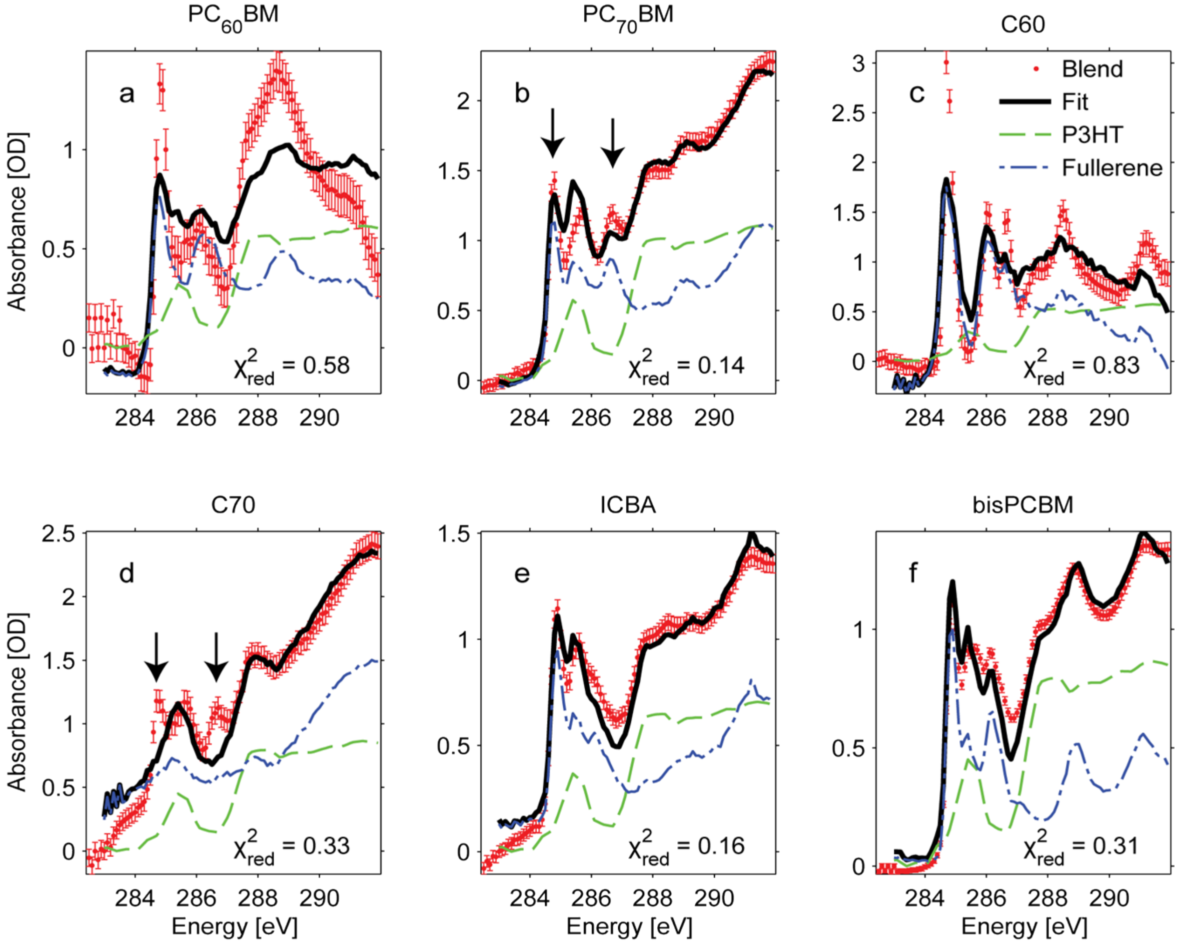

Figure S4. Examples of fitting linear combinations of NEXAFS spectra of pristine P3HT and fullerenes to P3HT-fullerene blends. The fits shown are the expected match e.g. a linear combination of P3HT and PC$_{60}$BM spectra to the P3HT-PC$_{60}$BM spectrum (a) P3HT-PC$_{60}$BM, (b) P3HT-PC$_{70}$BM, (c) P3HT-C60, (d) P3HT-C70, (e) P3HT-ICBA and (f) P3HT-bisPCBM. For each fit the reduced chi square is shown in the lower right corner. It is noticed that the spectrum from the C70 fullerene (blue line) most likely is from contamination and not actual sample since it lacks two prominent peaks (marked with black arrows) found in P3HT-C70, PC$_{70}$BM, P3HT-PC$_{70}$BM, C60 and P3HT-C60.

Reduced chi square	PC60BM	PC70BM	C60	C70	ICBA	BisPCBM
P3HT-PC60BM	**0.58**	0.97	**0.54**	1.00	0.97	0.76
P3HT-PC70BM	0.68	**0.14**	0.92	1.13	0.57	0.62
P3HT-C60	1.01	1.63	**0.83**	2.82	2.12	1.63
P3HT-C70	0.63	**0.21**	0.70	0.33	0.35	0.53
P3HT-ICBA	0.34	**0.15**	0.58	1.01	**0.16**	**0.13**
P3HT-BisPCBM	0.59	0.72	1.33	3.14	0.95	**0.31**

Table S5. The NEXAFS spectra of the P3HT-fullerenes mentioned in the left side have been fitted with a linear combination of the P3HT spectra and the spectra of the fullerene stated at the top. The reduced chi square of each linear combination is shown and the most likely combinations have been marked.

Degradation mapping of T100 P3HT and thickness artefacts in NEXAFS spectra

To have a good quality NEXAFS spectrum it is important to have a proper sample thickness compared to the beam intensity. For areas with very thin or no sample the optical density will effectively be zero since no photons are absorbed. For very thick sample areas there will be full photon absorption, which will result in few or no counted photons, high uncertainty and a disturbed spectrum. For the degradation maps it is only possible to accurately map sample areas with a proper photon count i.e. not identical to the incident beam and not close to zero. For the degradation maps both very thick and very thin areas were removed. As an example figure 1 shows 3 spectra from regions in P3HT T100; 1) no sample, 2) thin sample and 3) very thick sample. The figure demonstrates how the cut areas do not represent accurate P3HT spectra and should not be assigned a degradation level.

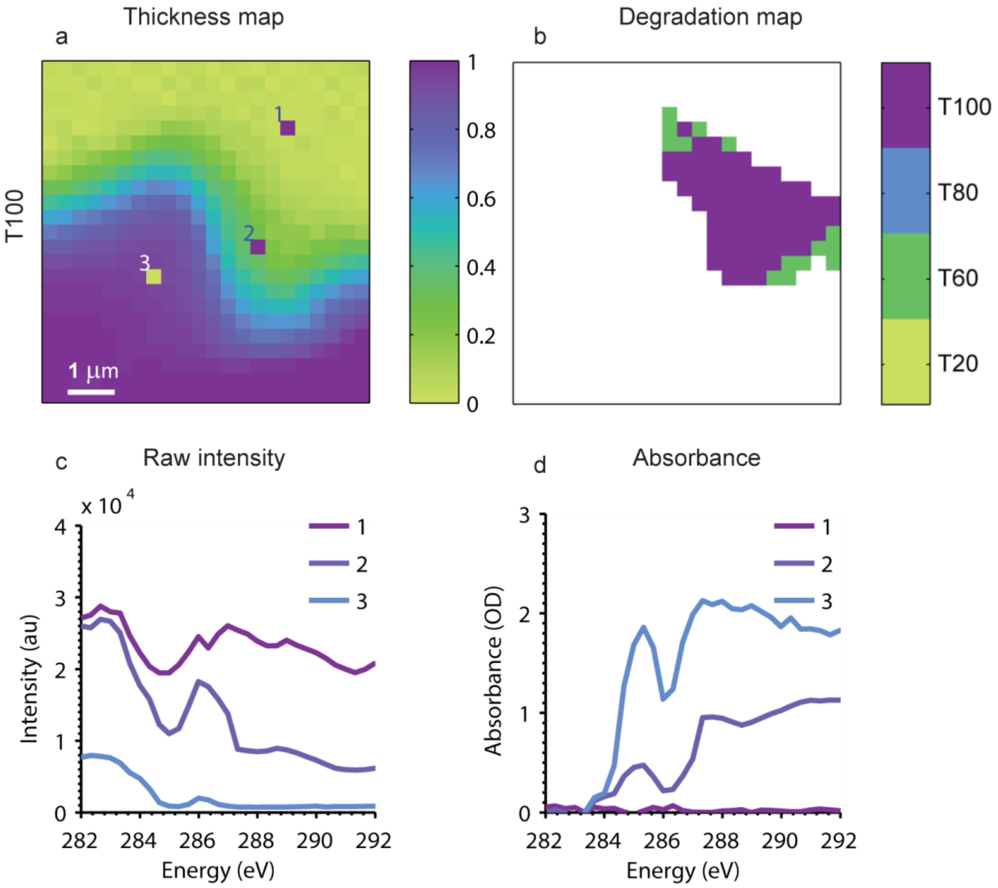

Figure S6. NEXAFS spectra from a P3HT T100 sample showing examples of too thick areas of a sample. (a) STXM map at 286 eV marking 3 positions, where the measured intensity spectra are shown in (c) and converted to optical density in (d). In (b) the homogeneous degradation map is shown. The raw intensities in (c) are the detected photon signal after sample penetration. (1) shows the beam line intensity, (2) shows an example of an acceptable absorbance (3) shows a thick area with mostly full absorption i.e. detected signal is near zero. For the optical density in (d) we see that the point without sample (1) correctly have an optical density of 0. The thick sample (3) has a disturbed signal which distorts the relative peak height and the last part of the spectrum, whereas the thin P3HT sample (2) provides an acceptable spectrum.

References

1. T. Tromholt, M. V. Madsen, J. E. Carlé, M. Helgesen, and F. C. Krebs, *J. Mater. Chem.*, 2012, **22**, 7592.