Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Morphological and electrical control of fullerene dimerization determines organic photovoltaic stability

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Measurement of the charge transfer band

In order to investigate if dimerization causes a change in the CT energy, we measured Fourier transform current spectroscopy (FTPS) in a fresh and aged P3HT:PCBM solar cell cast from chloroform. While this system is prone to fullerene dimerization, no significant changes in the CT band around 1.2-1.4 eV are observed after degradation. This suggests that dimerization does not change the CT energy which is consistent with the fact that dimerization does not cause *Voc* losses. It is not clear whether an apparent increase of the tail states around 0.8 - 0.9 eV might be related to fullerene dimerization or if this observation is caused by another degradation effect occurring at the same time.

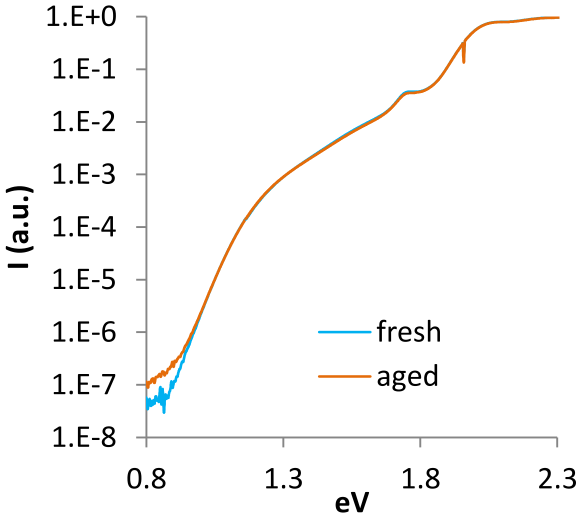


Figure S1: Fourier transform photocurrent spectroscopy measurements of a fresh and aged P3HT:PCBM solar cell cast from chloroform. Aging was performed in inert atmosphere under one sun equivalent white light illumination for ~40 h.

Addition of PCBM dimers that were isolated by HPLC to fresh devices

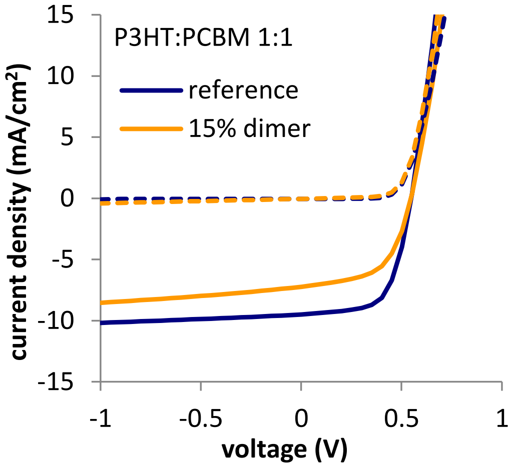


Table S1: Average device parameters for 8 P3HT:PCBM 1:1 reference devices and 8 devices with 15% dimer in the fullerene content as well as the relative losses by addition of dimerized fullerene.

	Jsc (mA/cm²)	PCE (%)	Voc (V)	FF (%)
reference	8.99	3.05	0.55	62.03
15% dimer	7.52	2.49	0.54	61.54
loss in %	16.4	18.3	1.6	0.8

Figure S2: IV curves of P3HT:PC60BM solar cells with 15% dimer in the fullerene content. PC60BM dimers were isolated with HPLC from photo-irradiated films.

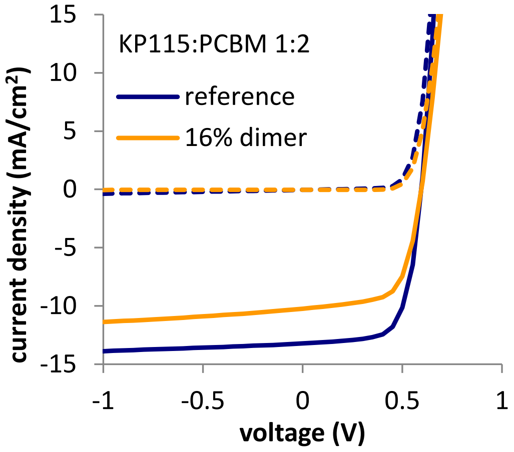


Table S2: Average device parameters for 11 KP115:PCBM 1:2 reference devices and 11 devices with 16% dimer in the fullerene content as well as the relative losses by addition of dimerized fullerene.

	Jsc (mA/cm²)	PCE (%)	Voc (V)	FF (%)
reference	13.39	5.20	0.60	64.54
16% dimer	9.85	3.83	0.59	65.53
loss in %	26.5	26.3	1.5	-1.5

Figure S3: IV curves of KP115:PC60BM solar cells with 16% dimer in the fullerene content.

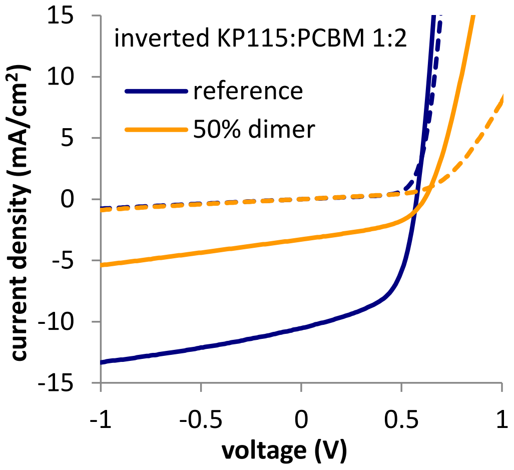


Table S3: Average device parameters for 10 inverted KP115:PCBM 1:2 reference devices and 10 devices with 50% dimer in the fullerene content as well as the relative losses by addition of dimerized fullerene.

	Jsc (mA/cm²)	PCE (%)	Voc (V)	FF (%)
reference	10.24	3.18	0.56	0.55
50% dimer	3.28	0.91	0.61	0.45
loss in %	67.9	71.3	-8.5	17.8

Figure S4: IV curves of inverted architecture KP115:PC60BM solar cells made with 50% dimers in the fullerene content.

HPLC measurements on active layer material from aged solar cells

In order to demonstrate the generality of the increased amount of dimers formed for solar cells aged at *Voc* conditions we provide data on several P3HT:PCBM solar cells. Some cells were aged under light intensities higher than one sun to improve the visibility of the effect. For comparability reasons, always two cells on the same substrate were measured, one held at *Jsc* and one at *Voc*.

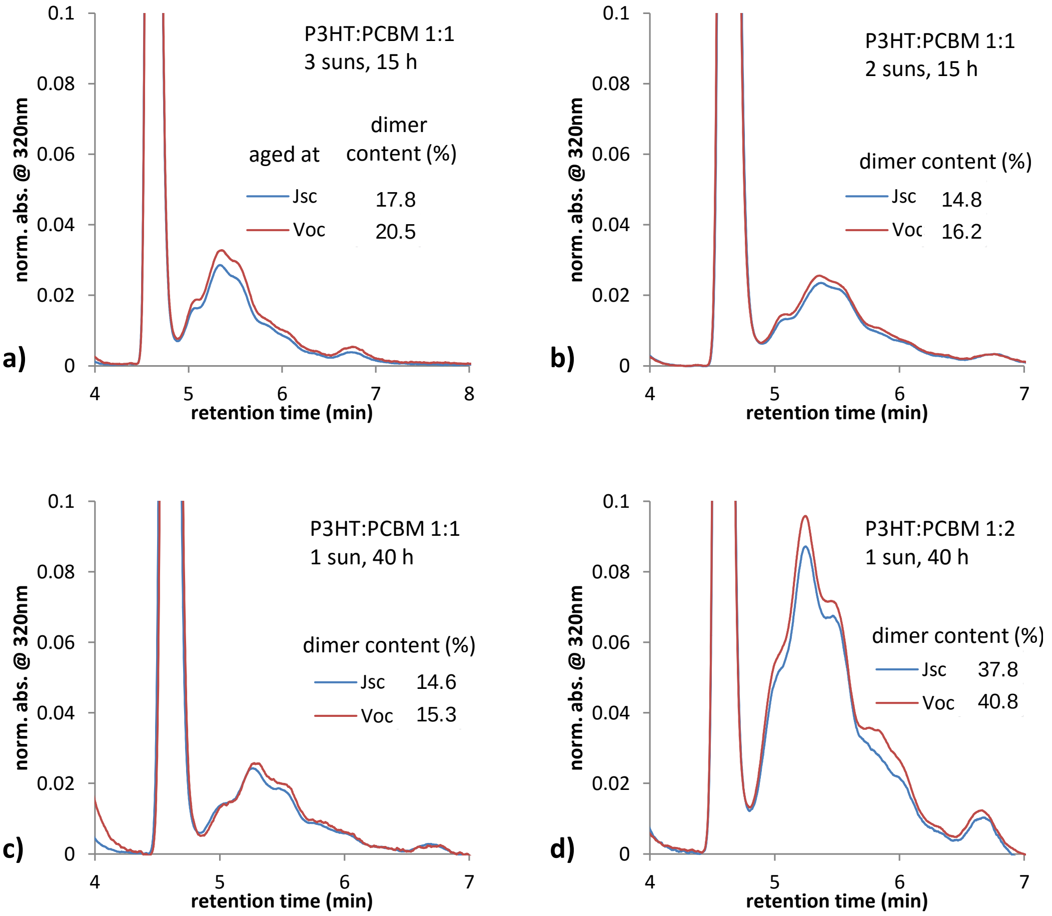


Figure S5: High performance liquid chromatography (HPLC) traces of P3HT:PCBM solar cells aged under different conditions. The active layer of each solar cell was scraped off after degradation, dissolved in toluene, filtered through a syringe filter (PTFE) and analyzed by HPLC (Cosmosil Buckyprep column; 4.6 mm x 250 mm; 1.0 mL/min toluene). We consistently observed an increased amount of dimer in solar cells aged under *Voc* conditions. The strong increase of dimer content for a polymer to fullerene ratio of 1:2 suggests that a large part of the fullerene forms pure domains that have a strong tendency to dimerize, see Figure 3 and 7 in the main paper.

Degradation curves

Three inverted architecture KP115:PC60BM solar cells on the same substrate were operated at open circuit, short circuit, and at the maximum power point during degradation. The cell aged under open circuit conditions shows the most severe performance losses with a *Jsc* decrease of over 30 %, whereas the cell aged under short circuit conditions has the smallest losses with 15 %.

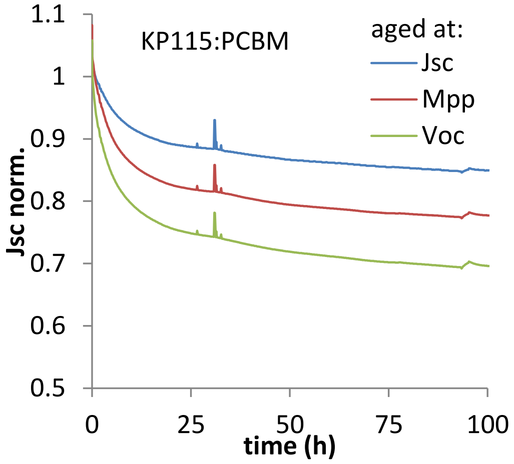


Figure S6: Photo-induced *Jsc* losses in inverted KP115:PC60BM solar cells show a strong dependence on the electrical bias during degradation. The light intensity during the test was monitored by a photodiode and changes less than 1%, except a spike at 30 h that transfers to the *Jsc* data.

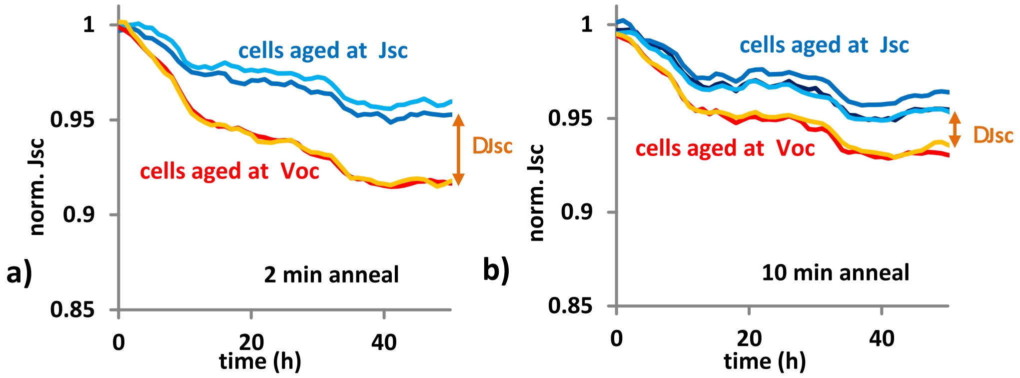


Figure S7: Degradation curves of multiple P3HT:PC60BM solar cells aged at *Jsc* and *Voc* conditions that were annealed for a) 2 min and b) 10 min. While the cells held at *Jsc* show comparable losses, the cells held at *Voc* show more degradation for an annealing time of 2 min. Those devices were built from the exact same solutions that were used to make films for GIXD measurements. All devices were aged under the same lamp and small fluctuations in the light intensity cause slight bumps in the curves.

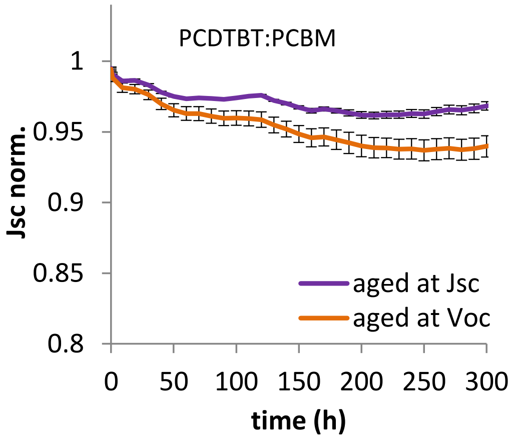


Figure S8: Normalized short circuit current of PCDTBT:PC60BM solar cells under illumination in inert atmosphere. A clear effect of the electrical bias on the performance losses can be observed. Averages of three devices each that were all aged under the same lamp are shown. Small fluctuations in the light intensity cause slight bumps in the curves.

EQE and Reflectance measurements

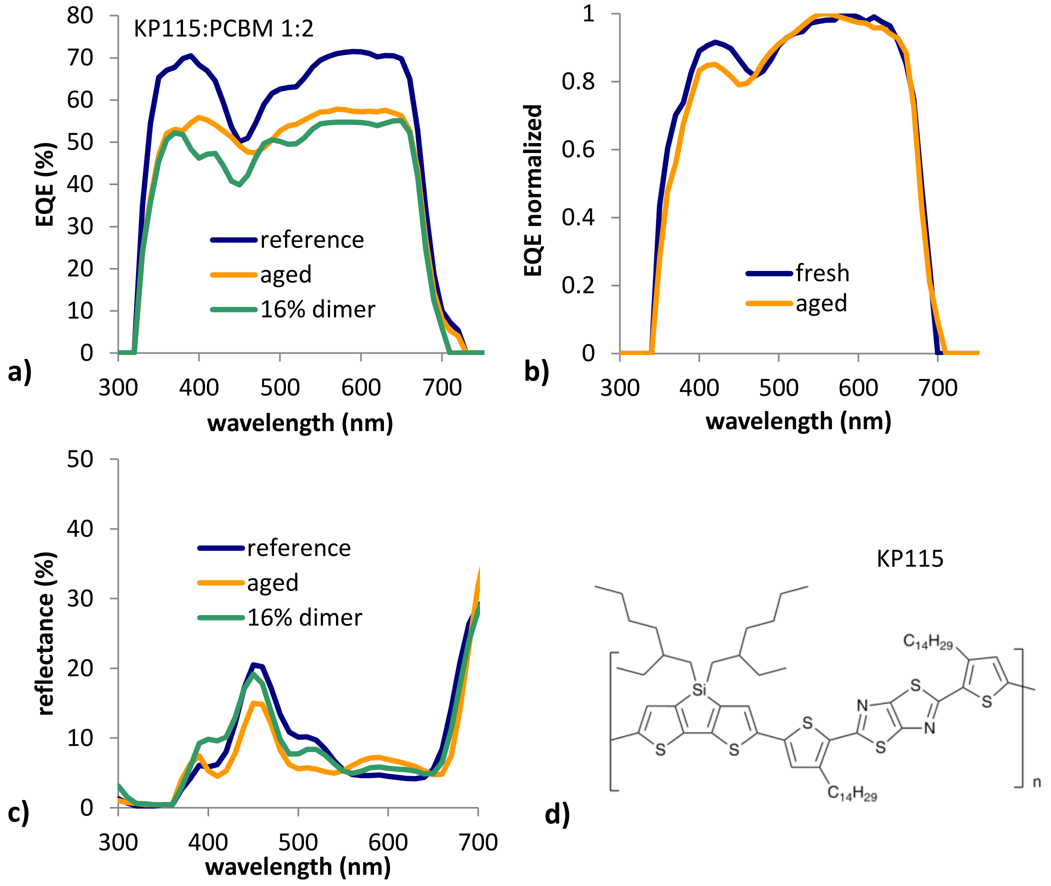


Figure S9: a) External quantum efficiency (EQE) of fresh and aged KP115:PC60BM solar cells and KP115:PC60BM solar cells where 16% dimer was added during cell production. b) Normalized EQE for fresh and aged KP115:PC60BM solar cells. A current reduction in the 350 - 450 nm regime where mainly fullerene absorbs is observed after degradation. This indicates incomplete exciton harvesting from fullerene domains. c) Reflectance measurements on aged solar cells and solar cells with 16% dimer do not indicate a significant decrease of absorption compared to the reference device. d) Structure of KP115, poly[4,4′-bis(2-ethylhexyl)dithieno[3,2-b:2′,3′-d]silole)-2,6-diyl- alt -[2,5-bis(3-tetradecylthiophen-2-yl)thiazole[5,4-d]thiazole)-1,8-diyl] (PDTSTzTz)

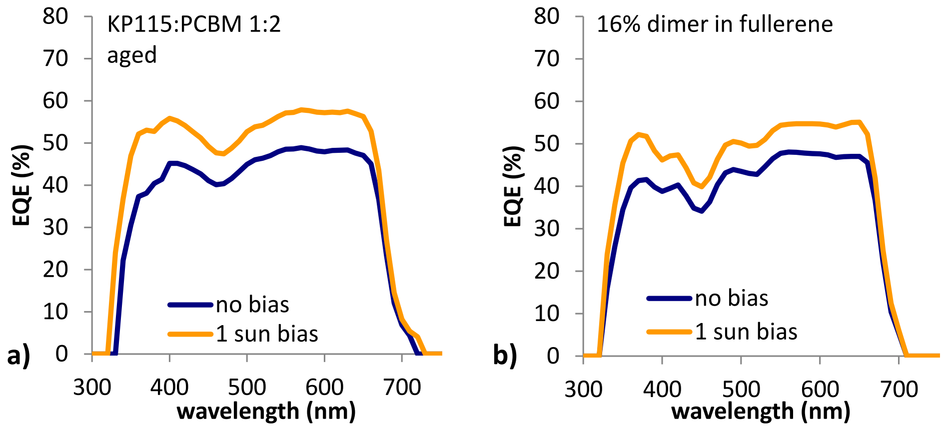


Figure S10: The EQE for a) aged KP115:PC60BM solar cells and b) solar cells with 16% dimer shows a strong increase under 1 sun equivalent light bias. This indicates transport limitations that are reduced by partial trap filling due to bias illumination.

Photoluminescence quenching measurements

A significant reduction of PCBM dimerization and photoluminescence is observed upon addition of 0.5 % PCPDTBT and above 5 % the PL signal is barely measurable. The PL signal of the neat fullerene film is centered at 740 nm and can be ascribed to the fluorescence emission from the S_1 singlet excited state of $PC_{60}BM$ (S. Cook, R. Katoh, and A. Furube, *J. Phys. Chem. C*, 2009, **113**, 2547–2552)

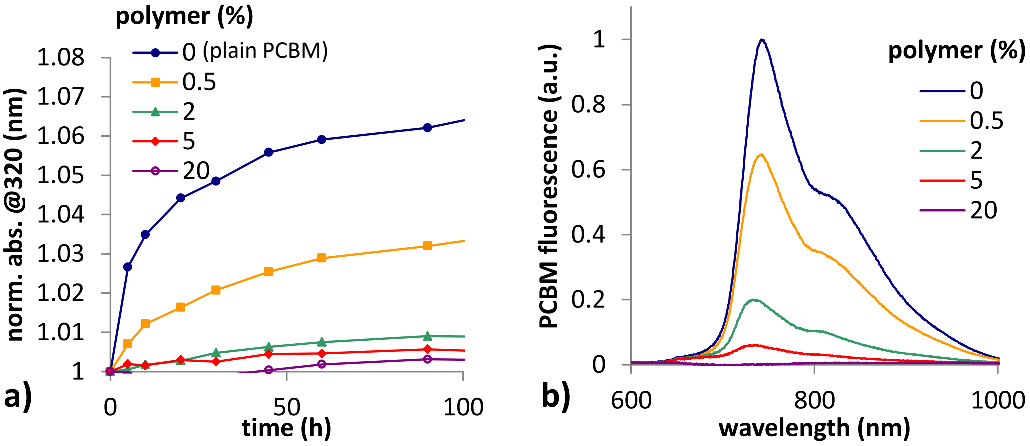


Figure S11: Influence of PCPDTBT content on a) dimerization of PCBM as measured by the change of absorption at 320 nm and b) PCBM luminescence quenching for an excitation at 405 nm.

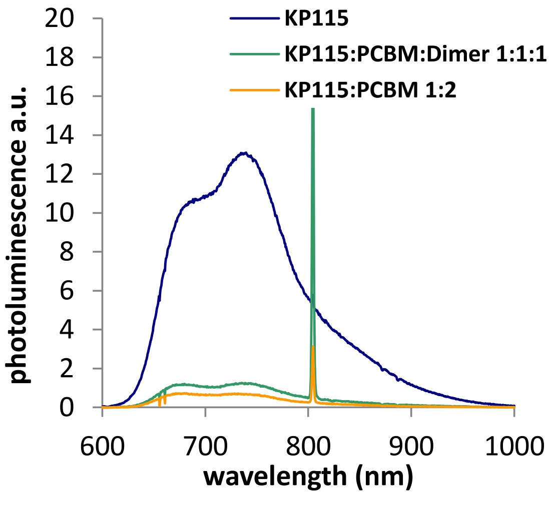
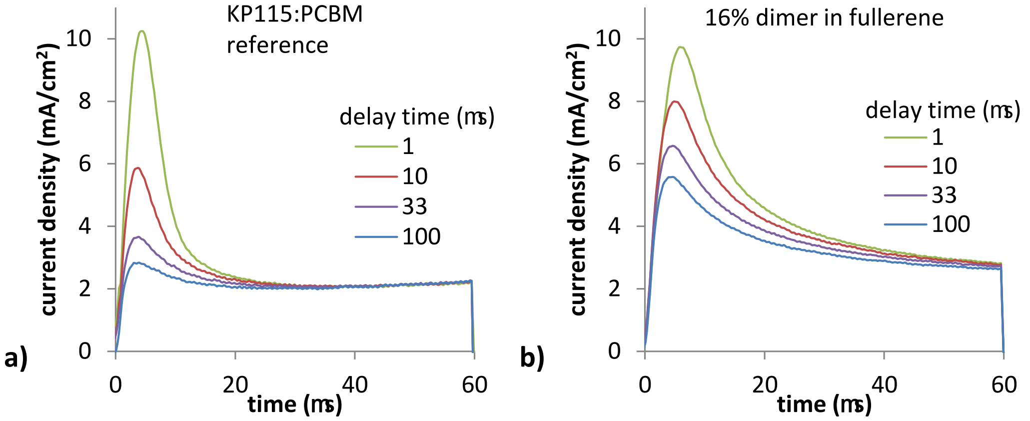


Figure S12: Photoluminescence measurements of polymer-fullerene blends with a 1:1 monomer to dimer mixture show increased photoluminescence compared to polymer- fullerene blends with only PCBM. This could indicate reduced exciton splitting at the polymer-dimer interface. But also morphological changes cannot be excluded. Excitation is at 529 nm and the spike at 805 nm an artifact from the used laser.

Charge transport measurements with photo-CELIV



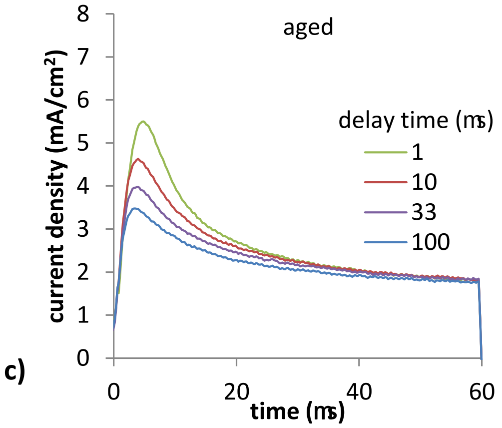


Figure S13: Raw photo-CELIV traces of KP115:PCBM solar cells show a clear peak broadening for devices with 16% dimer and for aged devices. This indicates dispersive transport, which means that there is a large fraction of carriers with an effectively lower mobility that leaves the device on longer times. While in the reference device the peak has largely disappeared after 100 µs delay time, there is still a significant peak present in the aged device and the device with 16% dimer. This means that a significant amount of charge carriers is left in the aged device after 100 µs and is a clear indication of trapping. Photo-CELIV was performed with a 405nm laser and an electronic switch to keep the solar cell at *Voc* during illumination and during the delay time.