Supporting Information

Elucidating the Mechanisms Underlying PCBM enhancement of $CH_3NH_3PbI_3$ Perovskite Solar Cells using GIXRD and XAFS

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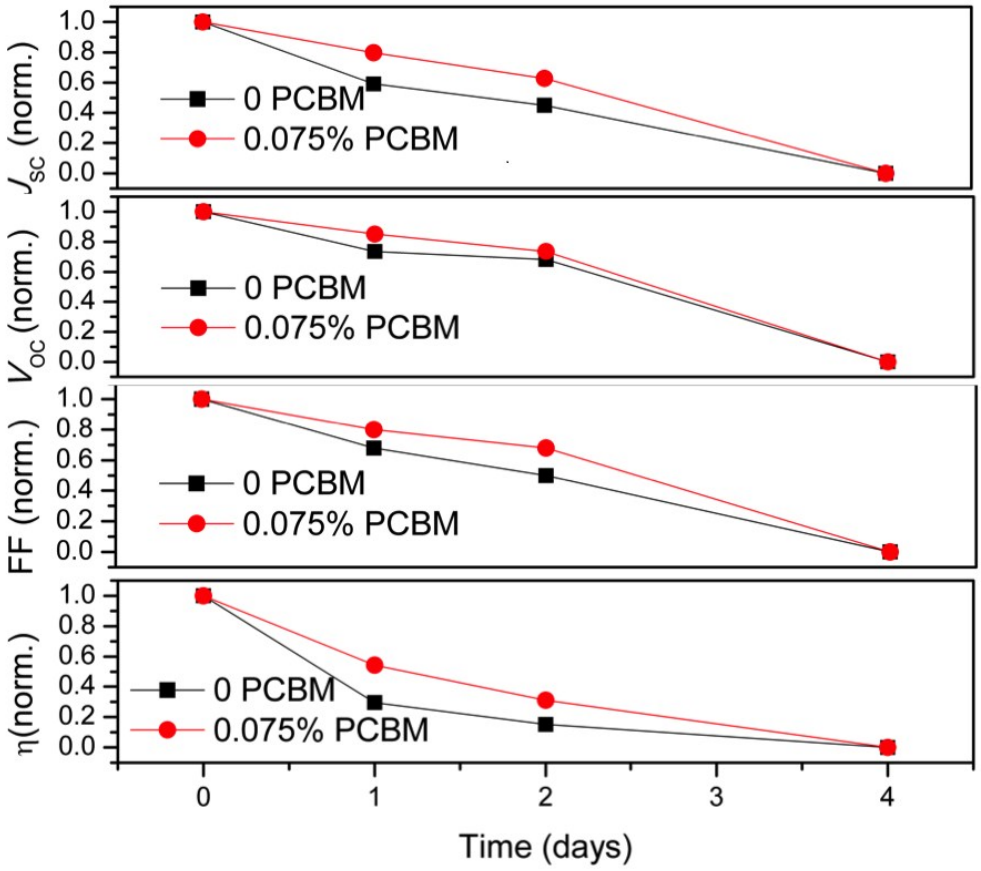

Figure S1. Stacked plot of the normalized performance parameters with time for devices of $MAPbI_3$ and 0.075% PCBM-doped $MAPbI_3$ stored in illumination.

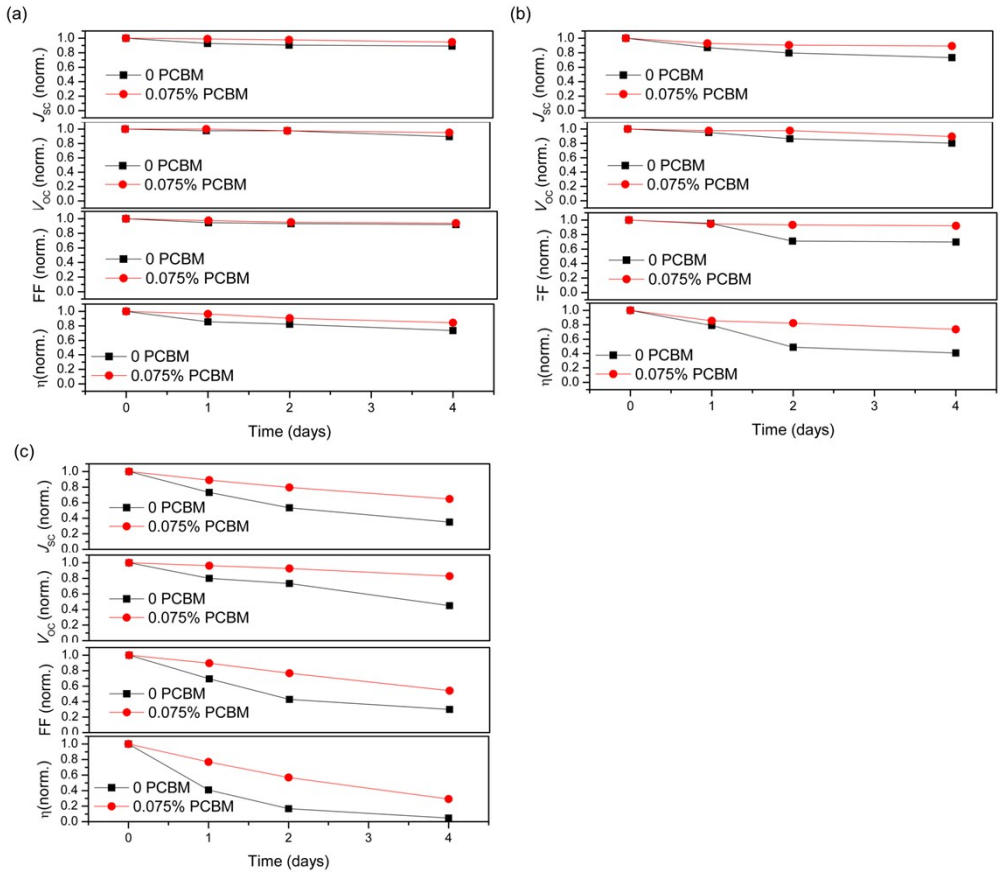

Figure S2. Stacked plot of the normalized performance parameters with time for devices of $MAPbI_3$ and 0.075% PCBM-doped $MAPbI_3$ stored in (a) 20% RH，(b) 50% RH and (c) 90% RH.

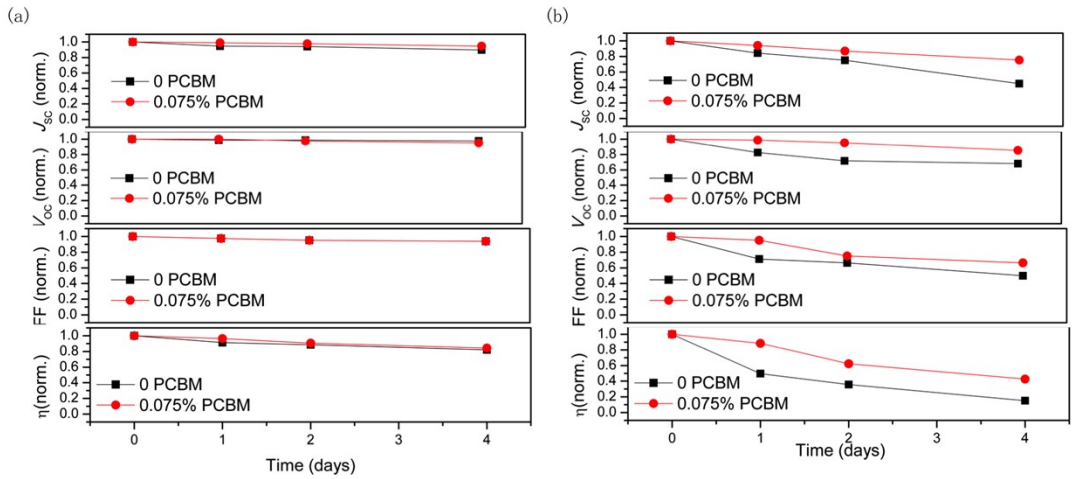

Figure S3. Stacked plot of the normalized performance parameters with time for devices of $MAPbI_3$ and 0.075% PCBM-doped $MAPbI_3$ stored in (a) 50℃and (b)85℃.

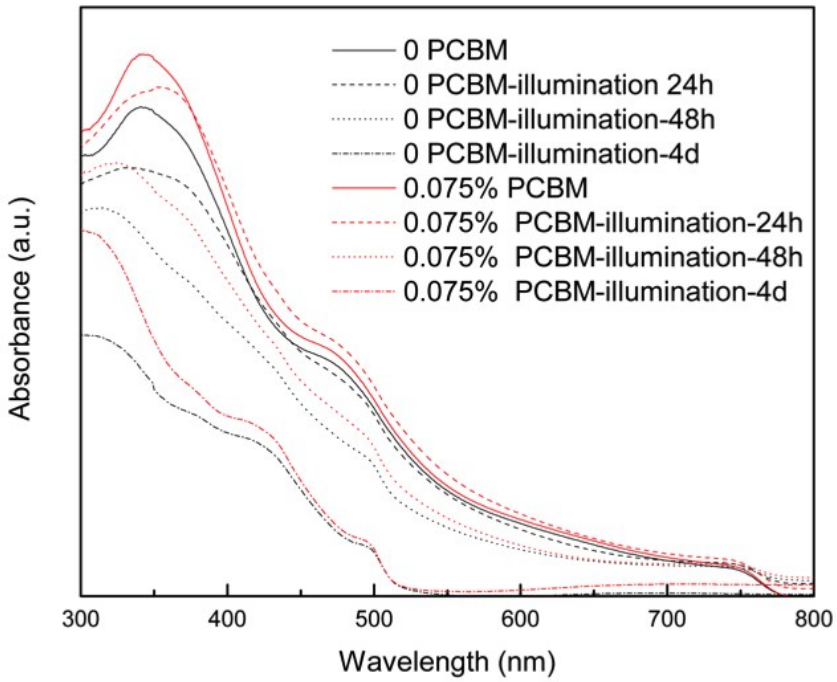

Figure S4. UV-Vis spectra of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after illumination.

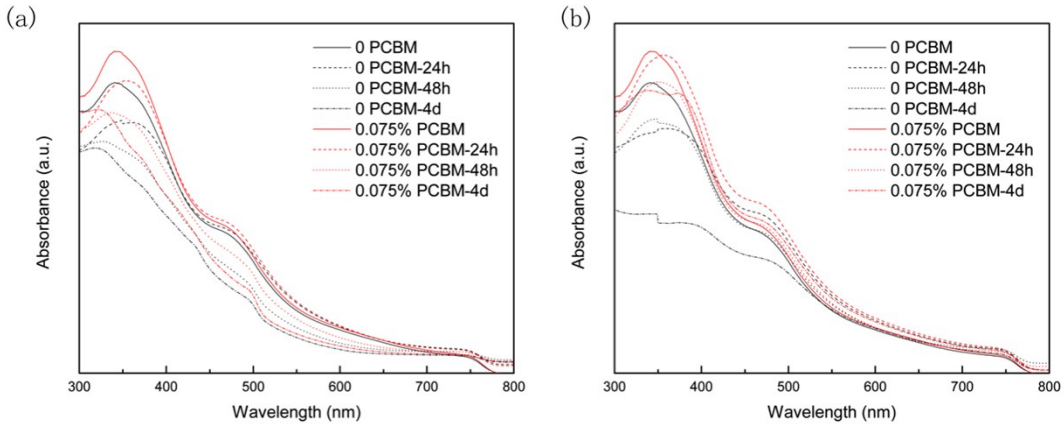

Figure S5. UV-Vis spectra of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after (a) 20% RH and (b) 50% RH.

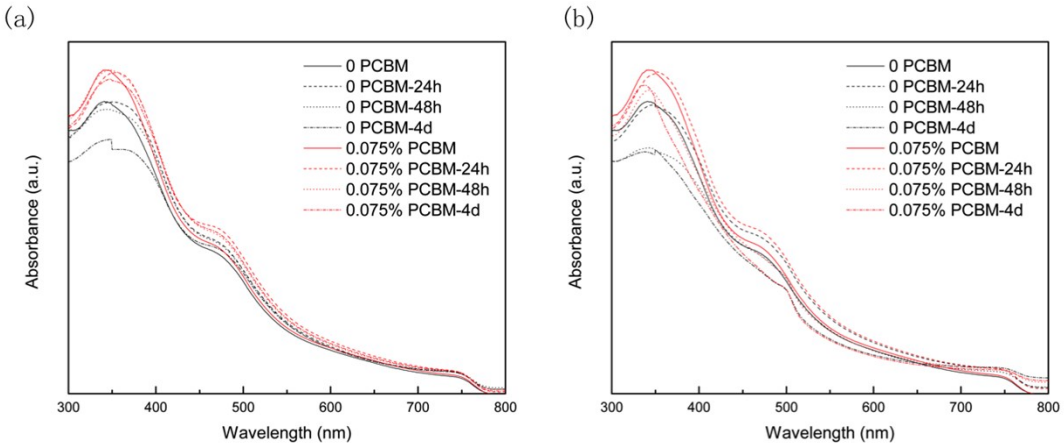

Figure S6. UV-Vis spectra of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after (a) 50℃ and (b) 85℃ treatment.

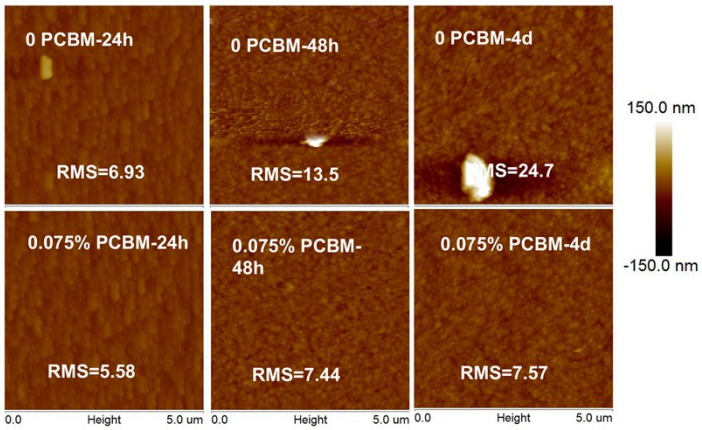

Figure S7. AFM images of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after illumination.

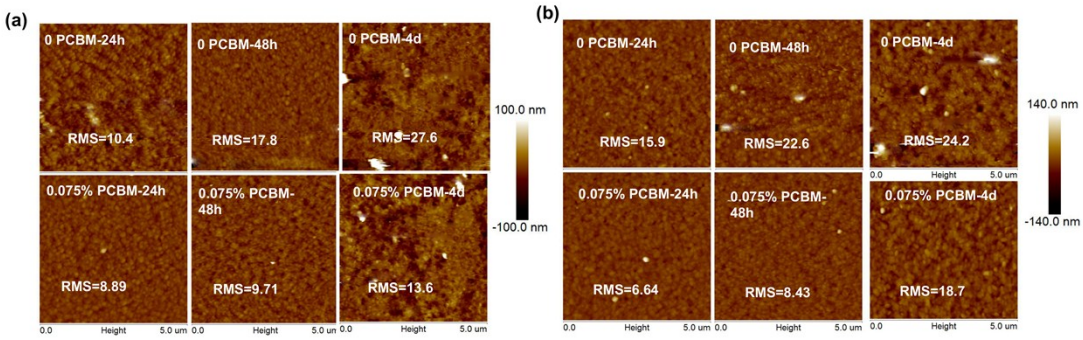

Figure S8. AFM images of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after (a) 20% RH and (b) 50% RH.

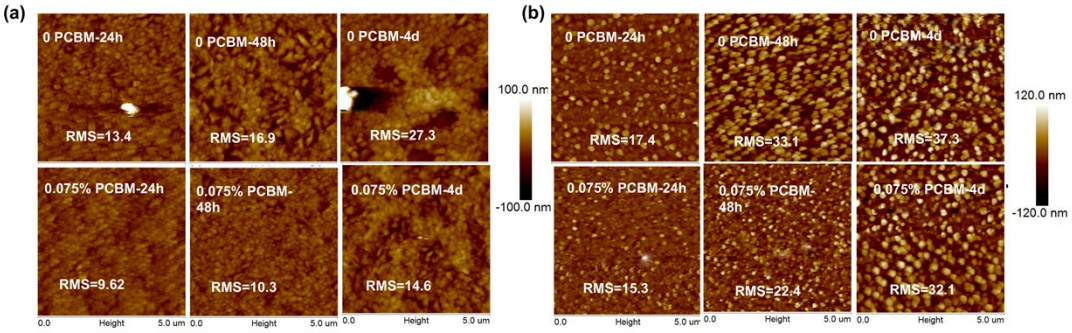

Figure S9. AFM images of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after (a) 50℃ and (b) 85℃ treatment.

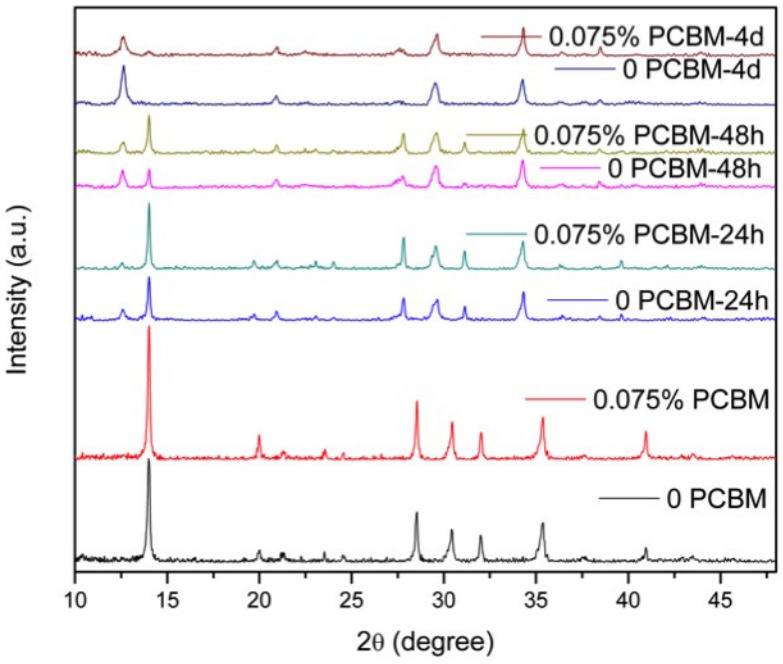

Figure S10. XRD patterns of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after illumination.

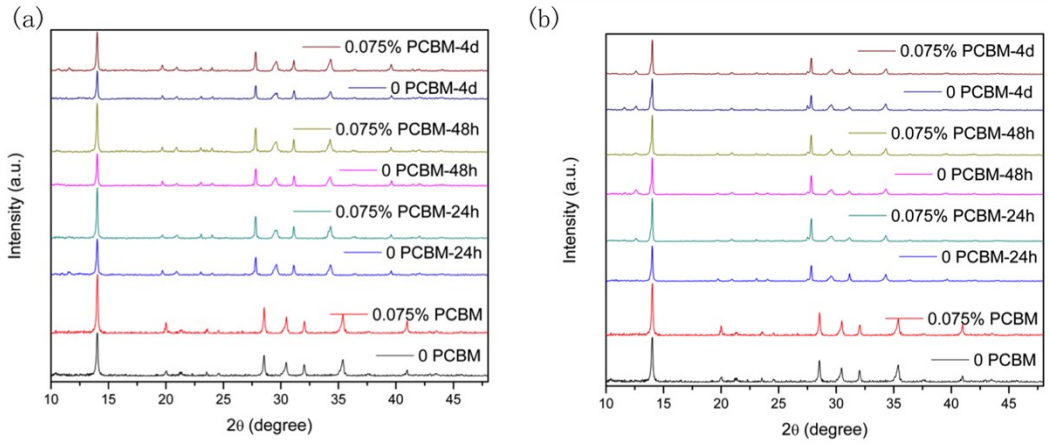

Figure S11. XRD patterns of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after (a) 20% RH and (b) 50% RH treatment.

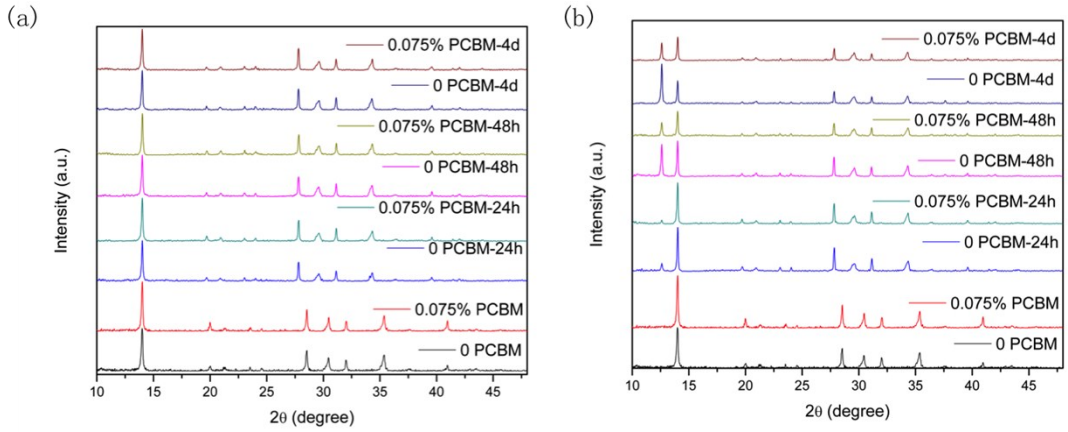

Figure S12. XRD patterns of the pristine $MAPbI_3$ film and the 0.075% PCBM-doped $MAPbI_3$ films after (a) 50℃ and (b) 85℃ treatment.

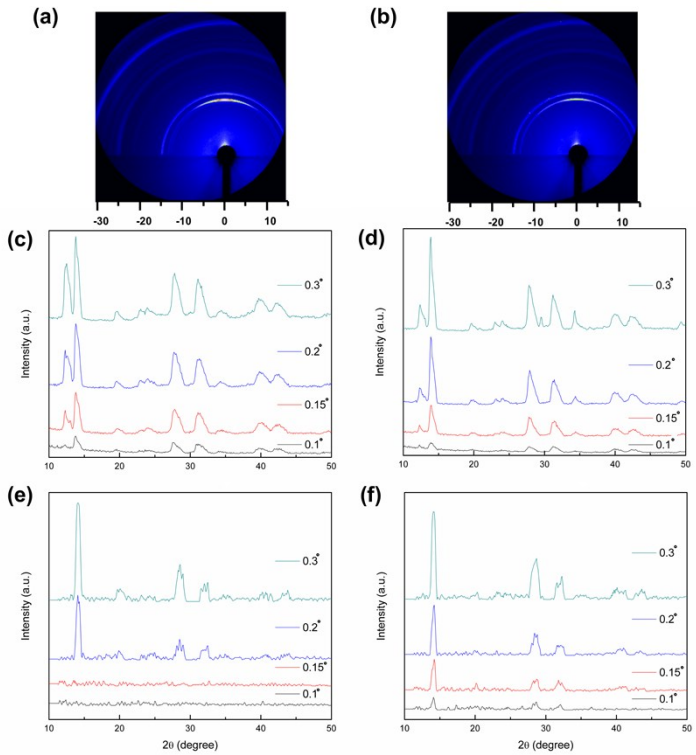

Figure S13. GIXRD patterns of the samples after illumination treatment. 2D-GIXRD profiles of (a) $MAPbI_3$ and (b) 0.075% PCBM-doped $MAPbI_3$ films. 1D-GIXRD profiles of (c) $MAPbI_3$ and (d) 0.075% PCBM-doped $MAPbI_3$ films obtained in OOP mode. 1D-GIXRD profiles of (e) $MAPbI_3$ and (f) 0.075% PCBM-doped $MAPbI_3$ films obtained in IP mode.

The depth of penetration of X-ray is:

$$L = \frac{\lambda}{2\pi\sqrt{{\alpha_C}^2 - sin^2\alpha_i}}$$

Therefore, by using three different incident angles of 0.1, 0.2 and 0.3°, we are able to reveal the structural difference in the perovskite films at a theoretical probing depth of ~30, ~200 and ~ 700nm, respectively. That is, the measured signal is only the information of the surface and near surface when the incident angle is 0.1°; the measured signal is basically the internal information of the thin films when the incident angle is 0.2°; and the measured signal is the diffraction information of whole films contained the thin films and substrate when the incident angle increase to 0.3°.

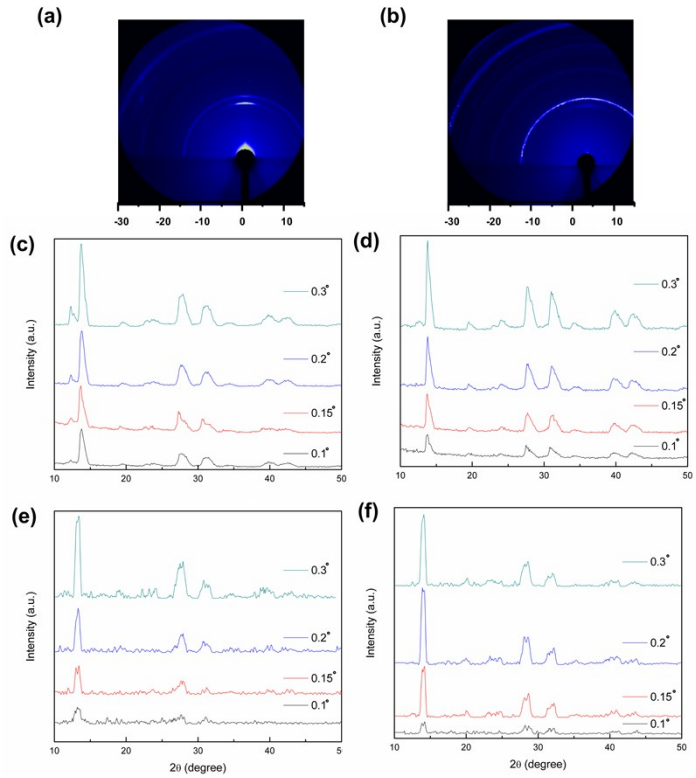

Figure S14. GIXRD patterns of the samples after 85℃ treatment. 2D-GIXRD profiles of (a) $MAPbI_3$ and (b) 0.075% PCBM-doped $MAPbI_3$ films. 1D-GIXRD profiles of (c) $MAPbI_3$ and (d) 0.075% PCBM-doped $MAPbI_3$ films obtained in OOP mode. 1D-GIXRD profiles of (e) $MAPbI_3$ and (f) 0.075% PCBM-doped $MAPbI_3$ films obtained in IP mode.

The figures of GIXRD patterns of the samples after other humidity (20% and 50% RH) and temperature (50℃) treatment are similar, but the variation degree is low.

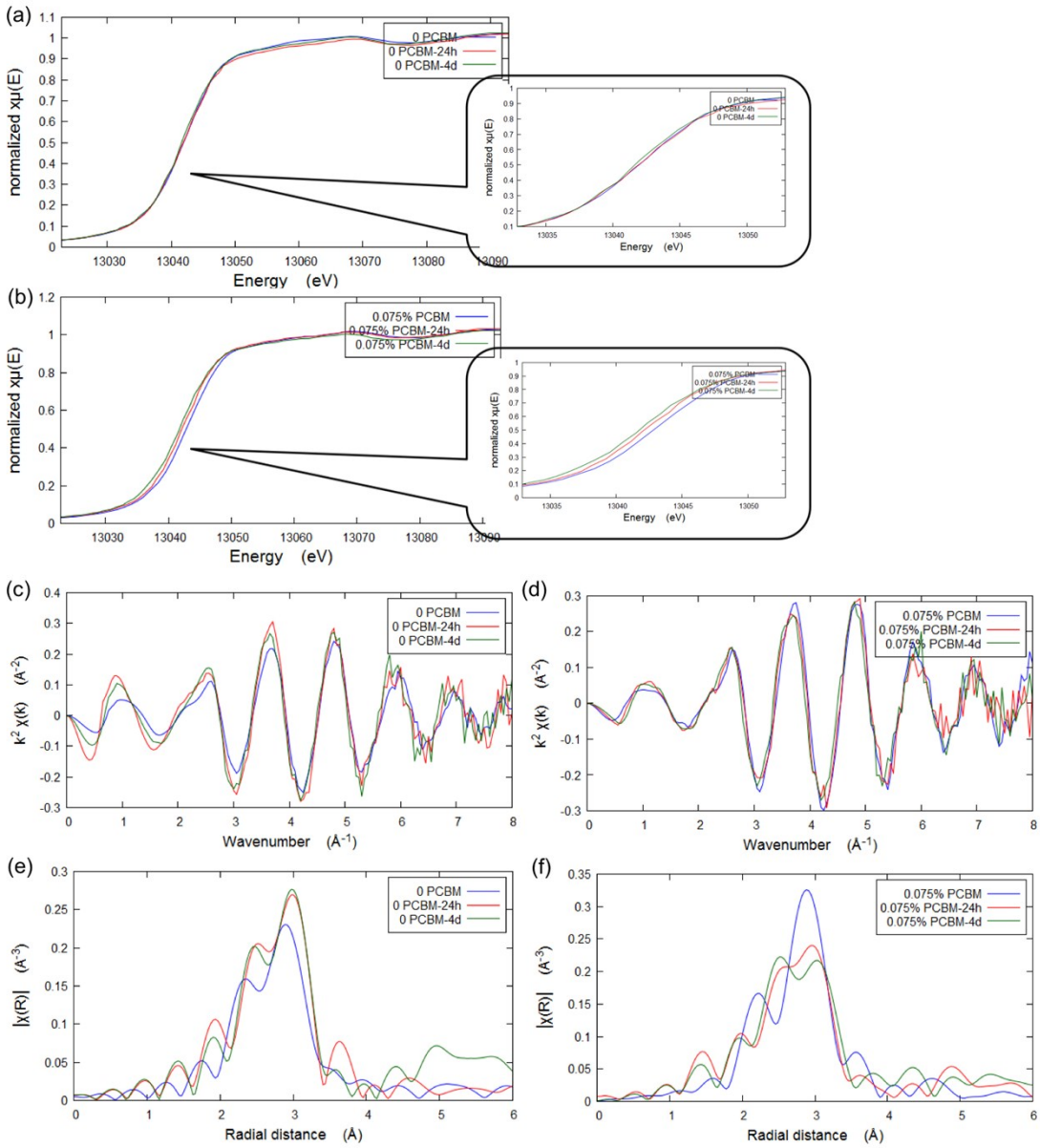

Figure S15. XAFS characterization of the samples after illumination treatment. Normalized Pb L_3-edge XANES spectra of (a) the pristine $MAPbI_3$ film, and (b) the 0.075% PCBM-doped $MAPbI_3$ film. k-weighted EXAFS spectra of (c) the pristine $MAPbI_3$ film, and (d) he 0.075% PCBM-doped $MAPbI_3$ film. Phase uncorrected FT of the EXAFS spectra of (e) the pristine $MAPbI_3$ film, and (f) the 0.075% PCBM-doped $MAPbI_3$ film.

The XAFS of the samples with different PCBM content (0.01%, 0.05%, 01% and 0.2%) are also tested, and if the PCBM content is too high (>0.1%), the change is similar to that of undoped film.

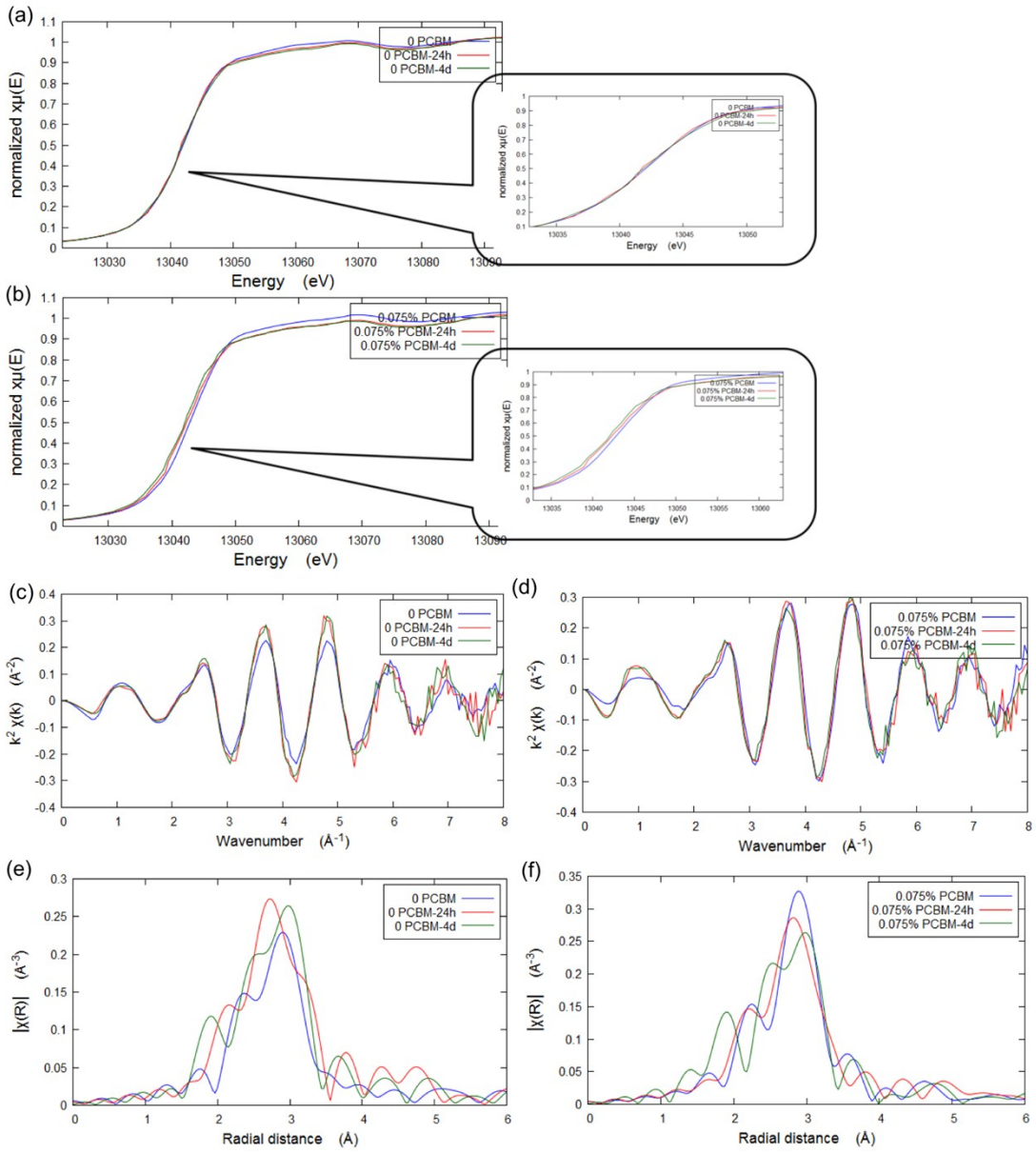

Figure S16. XAFS characterization of the samples after 85℃ treatment. Normalized Pb L_3-edge XANES spectra of (a) the pristine $MAPbI_3$ film, and (b) the 0.075% PCBM-doped $MAPbI_3$ film. k-weighted EXAFS spectra of (c) the pristine $MAPbI_3$ film, and (d) he 0.075% PCBM-doped $MAPbI_3$ film. Phase uncorrected FT of the EXAFS spectra of (e) the pristine $MAPbI_3$ film, and (f) the 0.075% PCBM-doped $MAPbI_3$ film.

The figures of XAFS characterizations of the samples after other humidity (20% and 50% RH) and temperature (50℃) treatment are similar, but the variation degree is low.

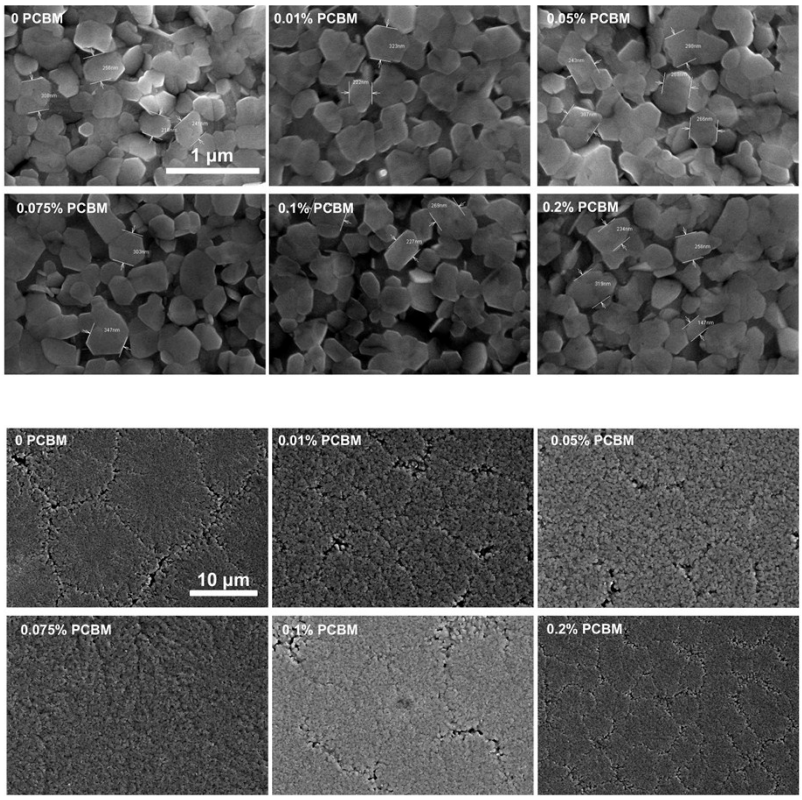

Figure S17. SEM images of the pristine $MAPbI_3$ film and the PCBM-doped $MAPbI_3$ films with different mass fraction of 0, 0.01%, 0.05%, 0.075%, 0.1% and 0.2% PCBM.

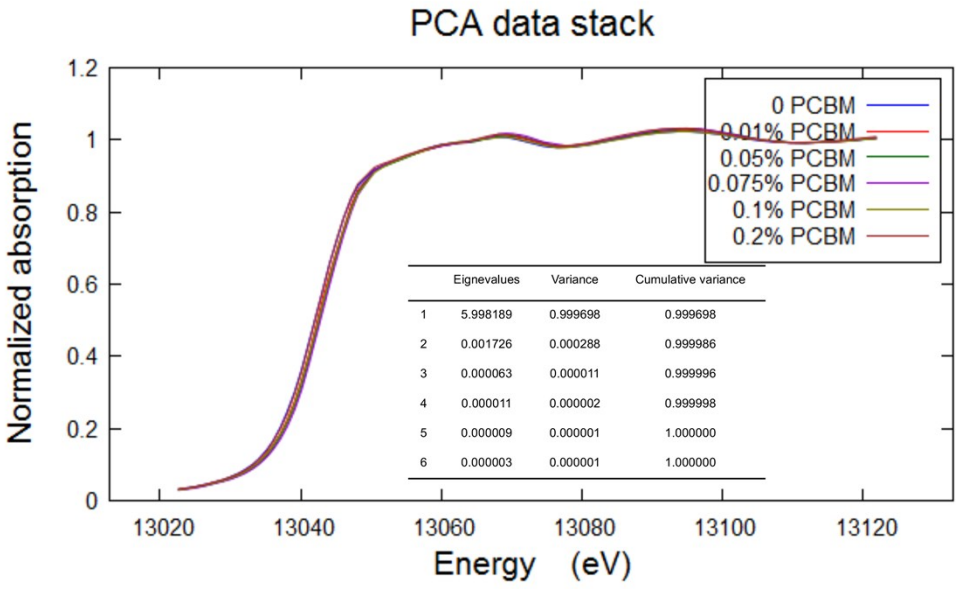

Figure S18. Reconstructed spectra of samples and PCA decomposition results.

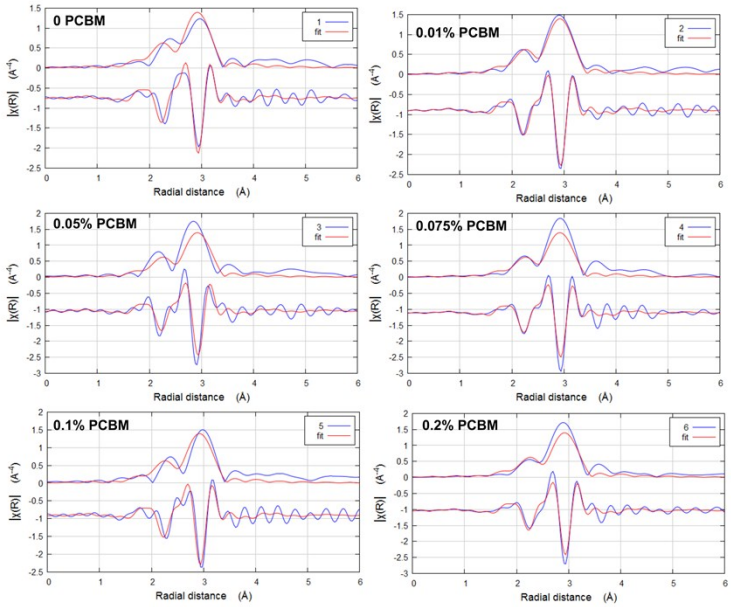

Figure S19. The fitting results of the Pb L_3 EXAFS by scattering from a single coordination shell of iodine.

Table S1. Photovoltaic parameters of perovskite solar cells made of $MAPbI_3$/PCBM active layer with different mass fraction of 0, 0.01%, 0.05%, 0.075%, 0.1% and 0.2% PCBM.

PCBM ratio [wt %]	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF	PCE [%]
0	20.28	0.97	0.67	13.18
0.01	21.22	0.96	0.75	15,28
0.05	22.08	0.96	0.77	16.32
0.075	23.44	0.98	0.80	18.38
0.1	21.25	0.97	0.70	14,43
0.2	18.29	0.95	0.64	11.12

Table S2. The changes in photovoltaic parameters of 0 and 0.075% PCBM-doped devices during 4 days under humidity (20%, 50%, 90%), illumination and heating (50℃, 85℃).

Treatment	0 PCBM				0.075% PCBM			
time	J_{SC}	V_{OC}	FF	PCE	J_{SC}	V_{OC}	FF	PCE
20% RH								

0h	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
24h	0.927	0.976	0.946	0.856	0.99	1.000	0.975	0.965
48h	0.904	0.976	0.932	0.822	0.976	0.976	0.950	0.905
4d	0.893	0.894	0.919	0.734	0.945	0.951	0.938	0.843
				50% RH				
0h	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
24h	0.872	0.951	0.953	0.790	0.927	0.976	0.946	0.856
48h	0.796	0.864	0.710	0.488	0.904	0.976	0.932	0.822
4d	0.732	0.802	0.696	0.409	0.893	0.894	0.919	0.734
				90% RH				
0h	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
24h	0.732	0.802	0.696	0.409	0.890	0.964	0.897	0.770
48h	0.535	0.735	0.428	0.168	0.797	0.928	0.769	0.569
4d	0.350	0.450	0.300	0.047	0.648	0.829	0.541	0.291
				illumination				
0h	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
24h	0.591	0.735	0.679	0.295	0.797	0.850	0.800	0.542
48h	0.450	0.680	0.50	0.153	0.626	0.735	0.679	0.312
4d	0	0	0	0	0	0	0	0
				50℃				
0h	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
24h	0.947	0.988	0.975	0.912	0.99	1.000	0.975	0.965
48h	0.941	0.988	0.95	0.883	0.976	0.976	0.950	0.905
4d	0.896	0.976	0.938	0.820	0.945	0.951	0.938	0.843
				85℃				
0h	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
24h	0.842	0.824	0.713	0.495	0.941	0.988	0.95	0.883
48h	0.75	0.718	0.663	0.357	0.87	0.951	0.75	0.621
4d	0.45	0.68	0.5	0.153	0.754	0.854	0.663	0.427

Table S3. The changes in absorption area calculated from UV-visible absorption spectra of 0 and 0.075% PCBM-doped devices during 4 days under

humidity (20%, 50%, 90%), illumination and heating (50℃, 85℃).

Treatment time	0 PCBM-doped	0.01% PCBM-doped	0.05% PCBM-doped	0.075% PCBM-doped	0.1% PCBM-doped	0.2% PCBM-doped
	586.7	597.5	604.3	631.8	625.5	572.3
			20% RH			
24h	553.1	560	574.5	614	536.8	530
48d	541.5	553.8	569.1	594.6	531.9	497.7
4d	357.9	469.2	475.9	514.3	466.4	465.1
			50% RH			
24h	500.8	541	565.3	571.2	551.8	526.4
48d	470.7	475.1	500.3	518.3	501.4	495.2
4d	350.7	366	451.7	585.8	526.3	363.1
			90% RH			
24h	481.7	488.1	488.2	518.2	494.1	457.9
48d	398.8	422	432.3	448.9	436.5	413.7
4d	213.9	260.2	397.1	408	405.3	309.9
			illumination			
24h	462.9	479.9	505.2	535.1	493	465.4
48d	369.7	387.8	414.8	420.6	415.7	371
4d	181.1	184.8	186.3	228.4	200.5	188.3
			50℃			
24h	521.7	554.3	555.8	558.6	544.4	515.2
48d	514.5	524.6	546.7	556.4	539.4	506.6
4d	474.3	522.7	540.6	548.3	507.4	481.5
			85℃			
24h	528.6	530.6	535.1	558	526.8	510.4
48d	462	467.7	480.2	505.8	486	431
4d	438.3	460.4	469.5	483.5	480	402.5

Table S4. The changes in root mean square (RMS) calculated from AFM images of 0 and 0.075% PCBM-doped devices during 4 days under humidity (20%,

50%, 90%), illumination and heating (50℃, 85℃).

Treatment time	0 PCBM-doped	0.01% PCBM-doped	0.05% PCBM-doped	0.075% PCBM-doped	0.1% PCBM-doped	0.2% PCBM-doped
	5.42	4.84	4.28	1329	3.54	4.93
			20% RH			
24h	10.4	10.2	7.37	8.99	9.3	10.1
48d	17.8	11.3	9.86	9.71	9.88	11.4
4d	27.6	16.2	16.5	13.6	15.6	18.2
			50% RH			
24h	15.9	10.9	7.66	6.64	15.2	19.5
48d	22.6	14.2	13.2	8.43	16.2	27.7
4d	24.2	22.2	18.9	18.7	18.9	29.4
			90% RH			
24h	29.3	21.5	19.1	16.0	21.8	35.4
48d	33.1	26.3	20.1	18.0	22.0	39.0
4d	84.9	71.1	38.9	31.6	52.0	163.0
			illumination			
24h	6.93	6.82	5.64	5.58	5.86	7.86
48d	13.5	11.8	8.82	7.44	11.3	12.4
4d	24.7	14.8	10.2	7.57	12.0	17.3
			50℃			
24h	13.4	12.8	9.98	9.62	10.9	11.8
48d	16.9	13.2	10.7	10.3	11.8	13
4d	27.3	17.2	17.1	14.6	18.1	19.8
			85℃			
24h	17.4	17.3	15.8	15.3	16.3	22.3
48d	33.1	29.2	29	22.4	22.8	29.3
4d	37.3	35	33.6	32.1	33.6	36.1

Table S5. The changes in the ratio of diffraction peak intensity of PbI_2 (100) to $MAPbI_3$ (110) calculated from XRD patterns of 0 and 0.075% PCBM-doped devices during 4 days under humidity (20%, 50%, 90%), illumination and heating (50℃, 85℃).

Treatment time	0 PCBM-doped	0.01% PCBM-doped	0.05% PCBM-doped	0.075% PCBM-doped	0.1% PCBM-doped	0.2% PCBM-doped
	0	0	0	0	0	0
			20% RH			
24h	2.7	1.9	0	0	0	1.5
48d	8.1	2.2	1.8	0	0	2.2
4d	11.4	6.6	2.1	0	0	4.4
			50% RH			
24h	9.7	6.4	5.7	2	3.7	5.4
48d	19.2	17.3	12.4	8.4	9.7	18.9
4d	27.3	22.5	16.6	10.8	11.1	23
			90% RH			
24h	23.4	14.3	7.6	1.4	2.7	8.9
48d	100.2	64.6	62.1	33.3	39.1	47.6
4d	311.5	261.8	245.7	85.0	96.8	155.5
			illumination			
24h	48.0	27.2	26.3	9.6	20.1	22.8
48d	156.9	122.7	99.4	50.7	75.6	126.7
4d			1010.1	830.4	857.9	988.3
			50℃			
24h	3.8	1.1	0.7	0	0	1.7
48d	6.4	3.5	1.2	0	1.3	2.7
4d	8.7	4	1.8	0.7	1.7	3.2
			85℃			
24h	22.9	15.8	12.9	7.7	8.8	26.1
48d	111.6	94.5	89.9	54.4	59.1	73.9
4d	184.5	135.0	125.5	80.8	161.3	347.8

Table S6. Parameters obtained from fitting the Pb L_3 EXAFS by scattering from a single coordination shell of iodine.

Sample	Atomic number, N	Amplitude damping factor, S_0^2	Debye-Waller factor, σ^2 ($Å^2$)	Bond length, *r* (Å)
0 PCBM	6	0.223	0.02021	3.1581 3.2624
0.01% PCBM	6	0.208	0.01844	3.1581 3.2624
0.05% PCBM	6	0.196	0.01707	3.1581 3.2624
0.075% PCBM	6	0.194	0.01636	3.1581 3.2624
0.1% PCBM	6	0.193	0.01639	3.1581 3.2624
0.2% PCBM	6	0.191	0.01593	3.1581 3.2624