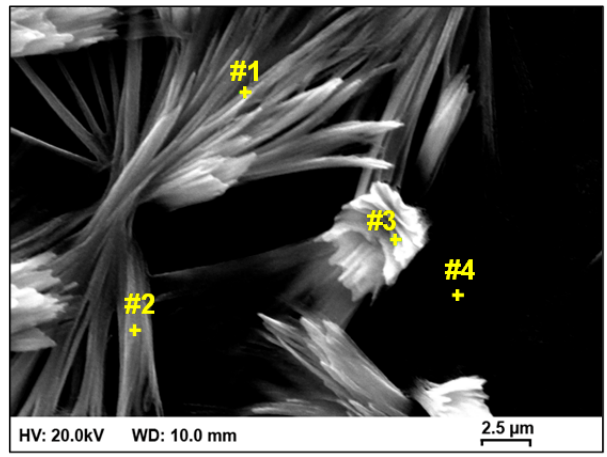
Supporting Information for

$CH_3NH_3PbI_3$ films prepared by combining 1- and 2-step deposition: How crystal growth conditions affect properties

Muhamad Z. Mokhtar[a,], Mu Chen[a], Eric Whittaker[c], Bruce Hamilton[c], Nicholas Aristidou[d], Simko Ramadan[a,b] Ali Gholinia[a], Saif A. Haque[d], Paul O'Brien[a,b], and Brian R. Saunders[a,]**

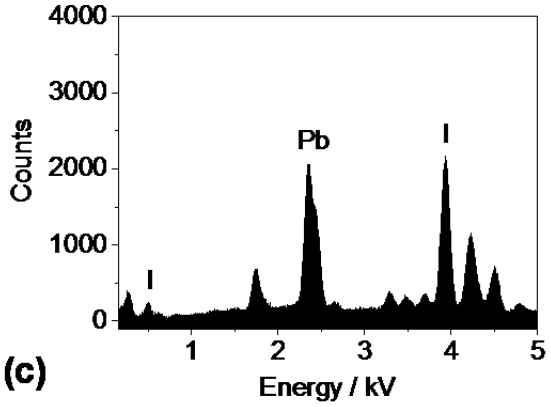
a) School of Materials, University of Manchester, MSS Tower, Manchester, M13 9PL, U.K.
b) School of Chemistry, University of Manchester, Manchester, M13 9PL, U.K.
c) Photon Science Institute, University of Manchester, Alan Turing Building, Oxford Road, Manchester, M13 9PL, U.K.
d) Department of Chemistry and Centre for Plastic Electronics, Imperial College London, South Kensington Campus, SW7 2AZ



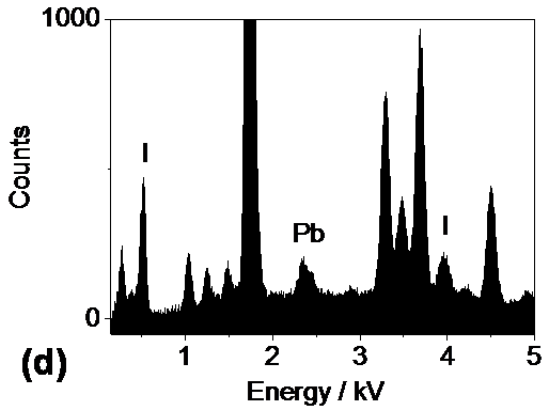
(a)

Position	Element	Atomic (%)
Point #1	Pb	32
	I	68
Point #2	Pb	31
	I	69
Point #3	Pb	31
	I	69
Point #4	Pb	27
	I	73

(b)



(c)



(d)

Figure S1. (a) SEM image of 1 & 2-s *precursor* film prepared using x = 0.66. The sample was analysed using EDX at the points shown. Points #1 to #3 correspond to the microcrystals. Point #4 probed the mp-TiO_2 layer containing 0.66MAPbI_3 and 0.34PbI_2 (i.e., 27.0 atomic% Pb^{2+}) according to Scheme 1a. For comparison PbI_2 contains 33 atomic% Pb^{2+}. (b) Table of atomic % values from the points shown in (a). EDX spectra for (c) Point # 1 and (d) Point #4. These data show that microcrystals (with nanocrystals at the surface) were Pb^{2+} rich compared to theory (27.0 mol.%) and Point #4.

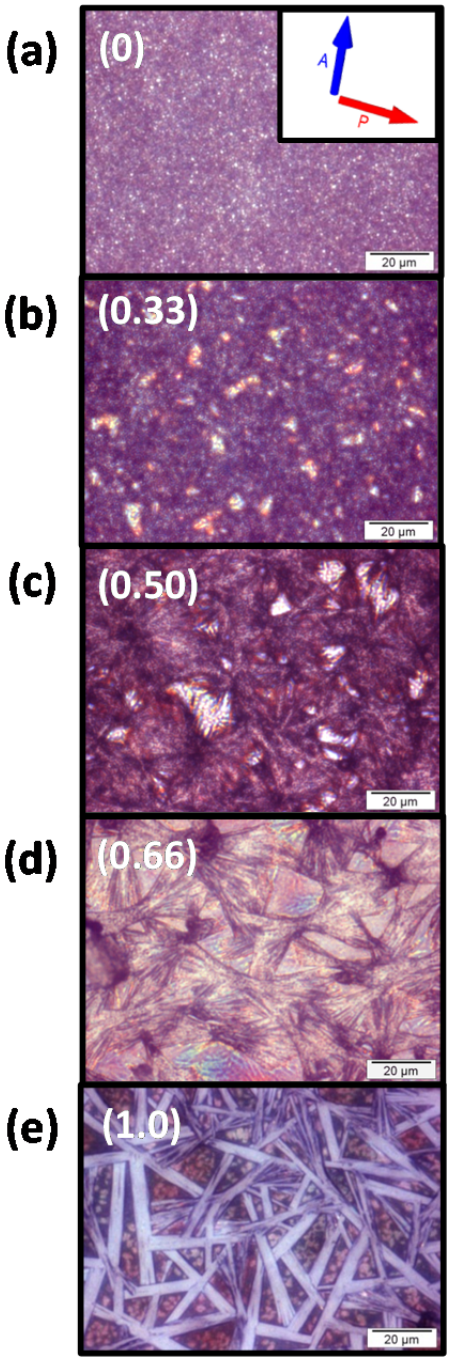


Figure S2 Polarised light optical microscopy images (a – e) for various *final* $MAPbI_3$ films prepared with different solution *x* values (shown). (a) and (e) correspond to 2-s and 1-s methods, respectively. (b) to (d) were prepared using the 1 & 2-s method. (See Scheme 1c) The inset for (a) shows the analyser (A) and polariser (P) directions used.

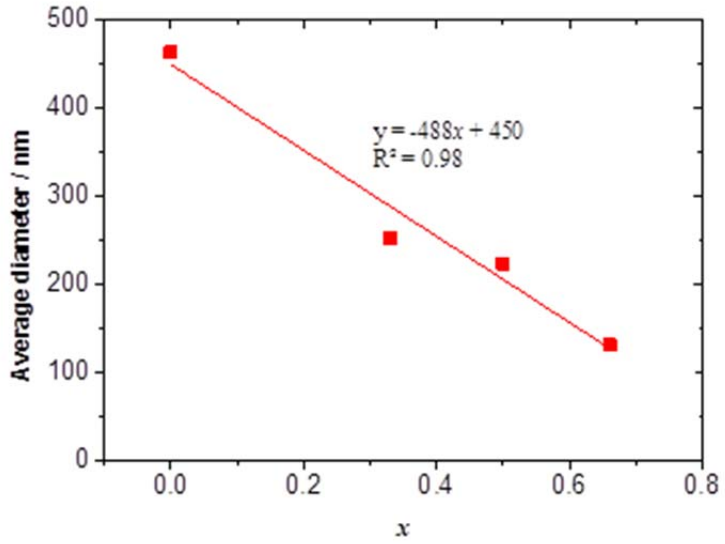


Figure S3 Effect of *x* for the PbI_2 + *x*MAI solutions used to prepare the precursor films on the average meso-crystal size for the *final* $MAPbI_3$ films shown in Fig. 1b. The combined 1 & 2-s method used *x* = 0.33, 0.50 and 0.66. Note that *x* = 0 corresponds to the 2-s method. Meso-crystals were not evident for the 1-s (*x* = 1.0) film.

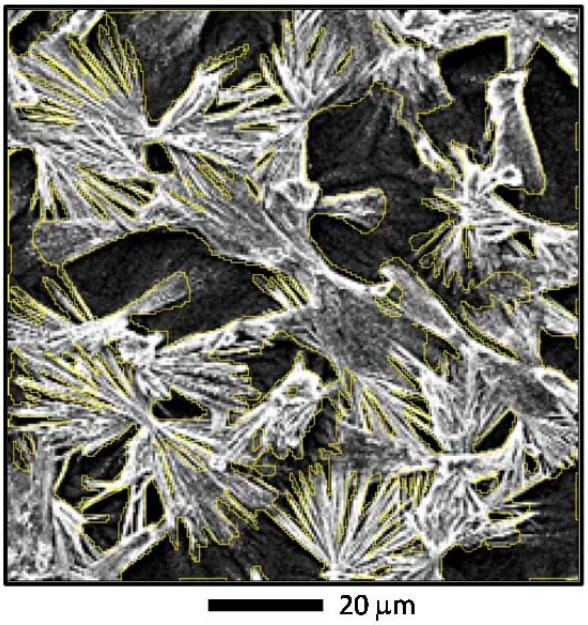


Figure S4. Example of image used for calculation of the % coverage. This SEM image was obtained for the *final* 1 & 2-s film prepared using x = 0.66 and is taken from Fig. 1b. The yellow outline was used to delineate the crystals from the background. The automated threshold was conducted using Image J software and included only the dark black areas (pinholes). The % coverage was determined by subtracting the total pinhole area from the total area of the image and normalising the difference with the total image area.

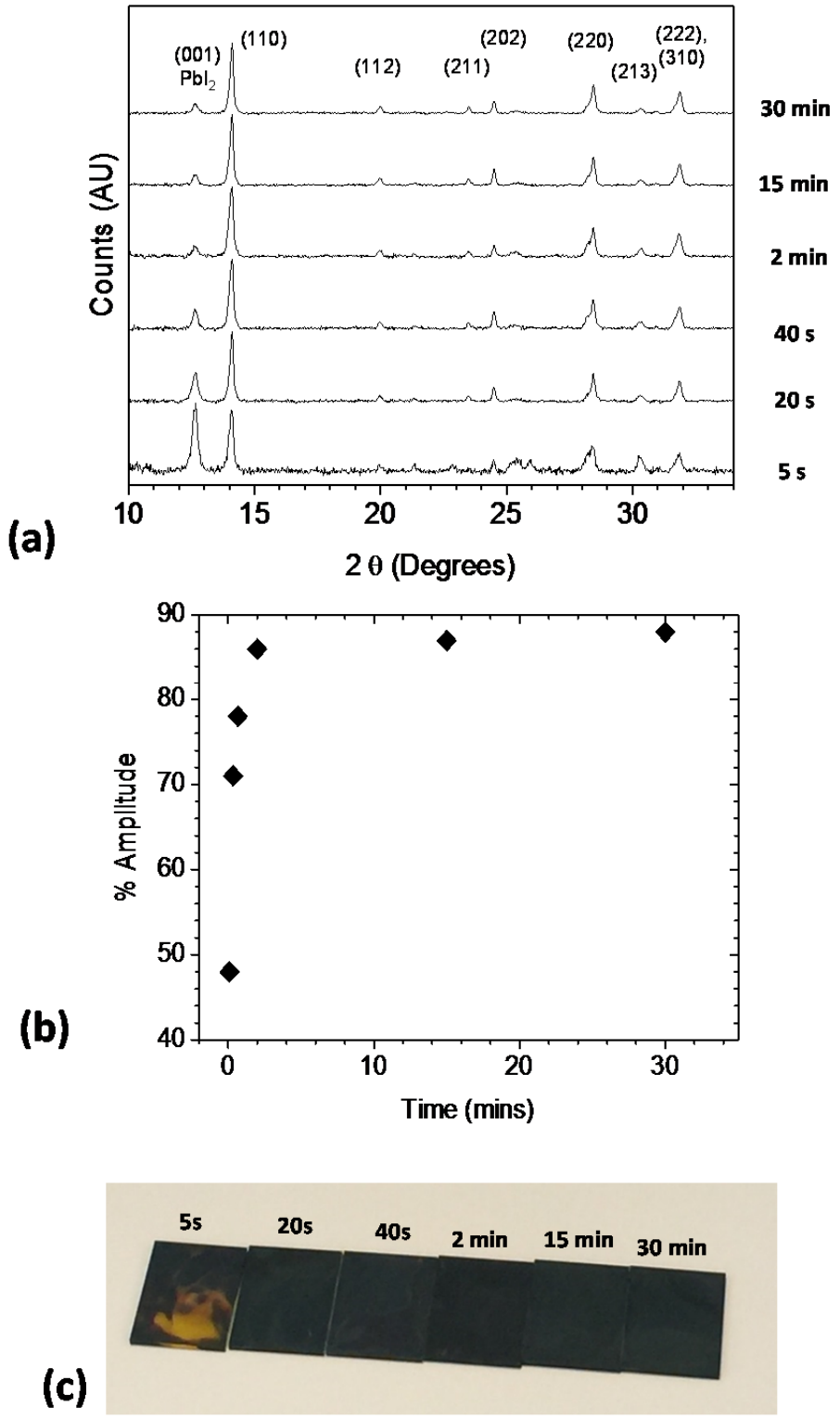
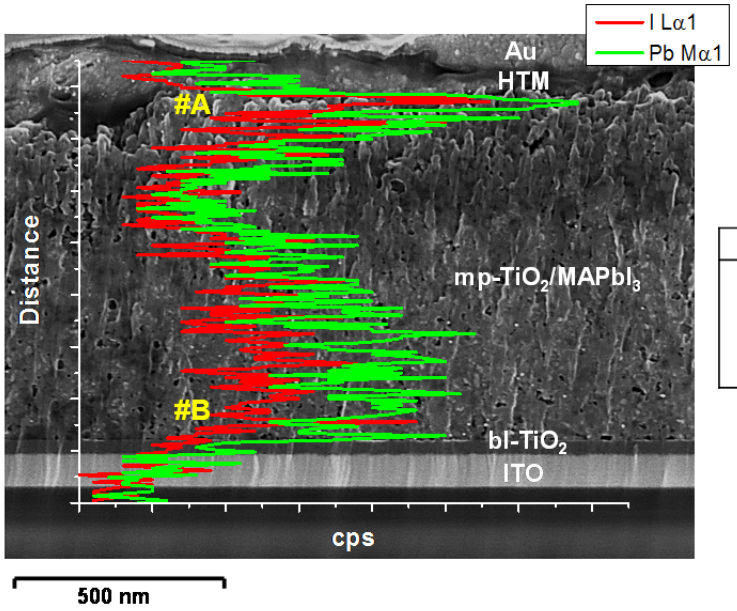


Figure S5 (a) X-ray diffractograms for *final* $MAPbI_3$ films prepared using the 2-s method (x = 0) – See Scheme 1b. The immersion time was varied as shown. (b) Variation of the % of amplitude of the $MAPbI_3$ (110) peak with x (see text). (c) Images of the films used for (a).



Position	Element	Atomic (%)
Point #A	Pb	18
	I	82
Point #B	Pb	33
	I	67

Figure S6. SEM cross section of an ITO/bl-TiO_2/mp-TiO_2/$MAPbI_3$/Spiro-MeOTAD/Au device that contained a $MAPbI_3$ photoactive layer prepared using the 1 & 2-s method (x = 0.5). EDX line scanning data are shown for Pb and I. The scanning was performed perpendicular to the film surface starting from the HTM. Points #A and #B probed the compositions near the surface and deep within the photoactive layer. The atomic % values measured for Points #A and #B are shown in the table.

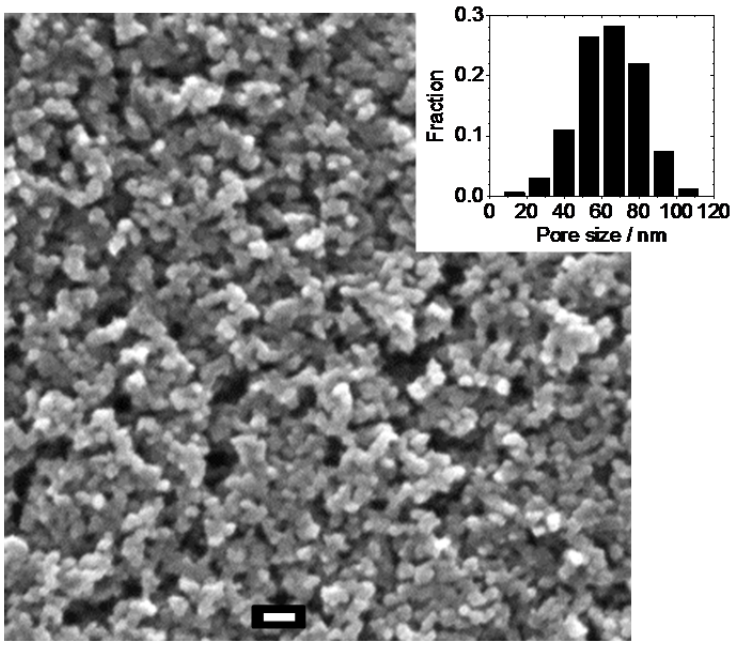


Figure S7 Representative SEM image for mp-TiO_2. The scale bar represents 100 nm. The pore size distribution is shown.

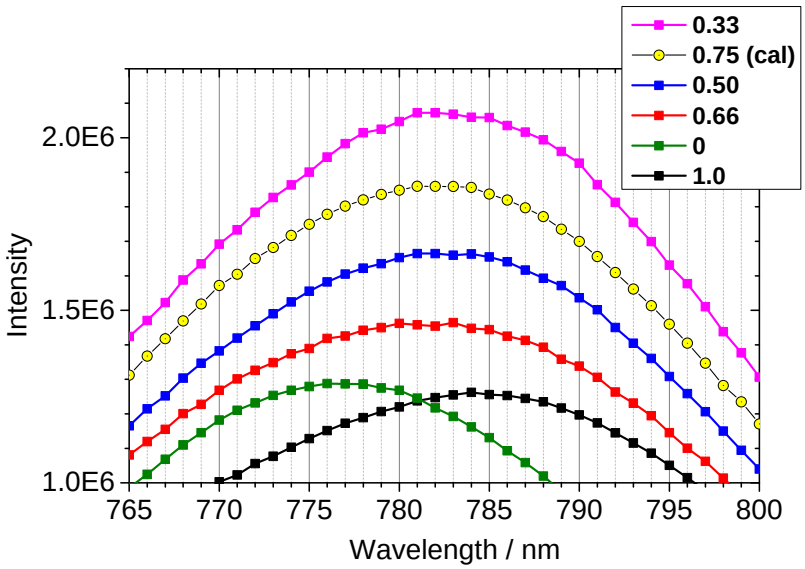


Figure S8 Expanded view of PL spectra for the final $MAPbI_3$ films from Fig. 5a. The values for x are shown in the legend. A calculated spectrum for x = 0.75 is shown which was obtained by using F = 1.5 x ($0.25F_0$ + $0.75F_{1.0}$) where F_o and $F_{1.0}$ are the measured fluorescence intensities for the x = 0 and 1.0 films, respectively.

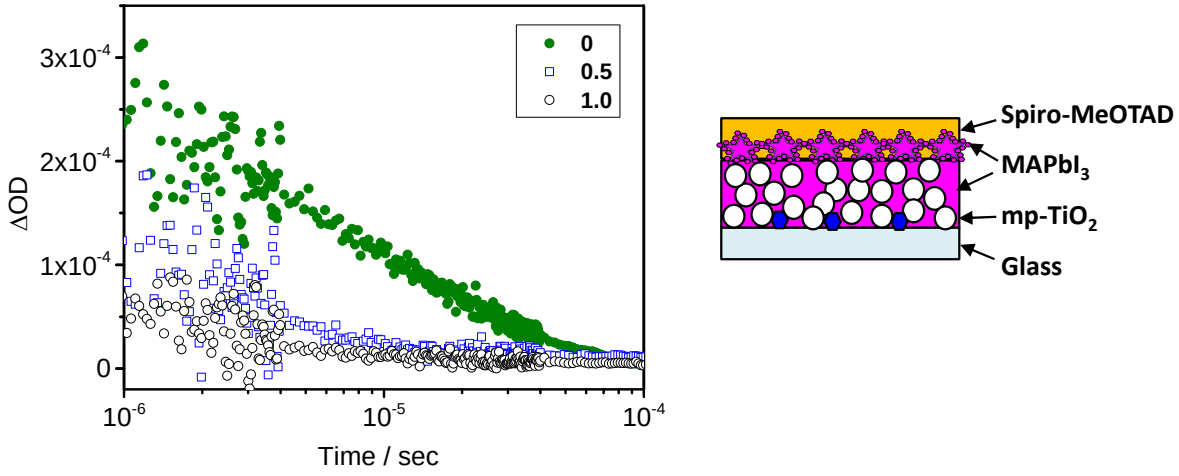


Figure S9. Transient absorption spectroscopy data for mp-TiO_2/$MAPbI_3$/*spiro*-MeOTAD. The legend shows the values for *x* used for the preparation of the films. The architecture of the device used for these experiments is also shown.

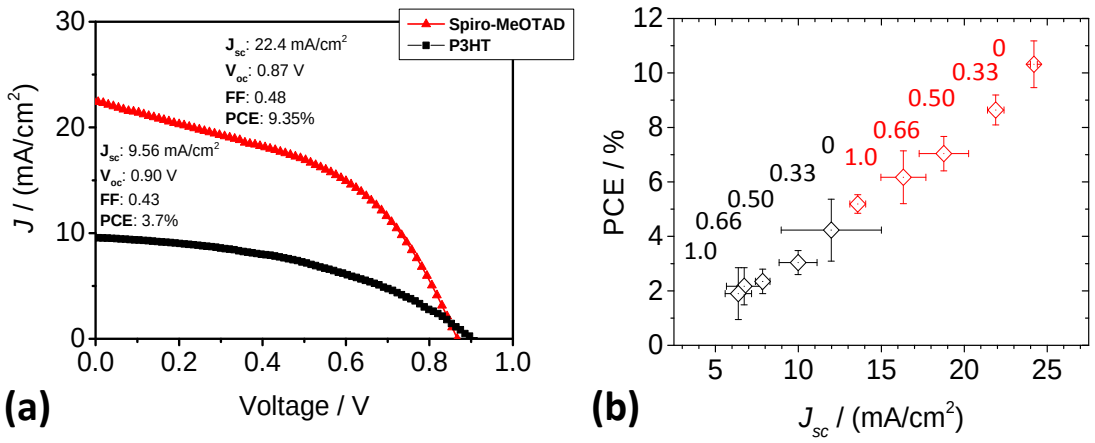


Figure S10 (a) *J-V* curve for the best 1 & 2-s (x = 0.33) cells. (b) Relationship between PCE and J_{sc} for devices prepared using P3HT (black open diamonds) or spiro-OMeTAD (red open diamonds) as the HTM.

Table S1: Photovoltaic performance data for perovskite devices measured using the forward scan.[a]

***x*MAI**	**HTM**	**J_{sc} ($mAcm^{-2}$)**	**V_{oc} (V)**	**FF**	**PCE (%)**	**Hysteresis (%)**
0	P3HT	11.98 ± 3.02	0.83 ± 0.09	0.39 ± 0.09	4.23 ± 1.14	15.1 ± 1.9
0.33		9.98 ± 1.14	0.84 ± 0.06	0.37 ± 0.05	3.04 ± 0.44	8.75 ± 0.88
0.50		7.85 ± 0.44	0.83 ± 0.03	0.36 ± 0.04	2.35 ± 0.45	6.60 ± 0.73
0.66		6.73 ± 1.07	0.81 ± 0.07	0.39 ± 0.05	2.17 ± 0.68	4.33 ± 0.52
1.0		6.38 ± 0.8	0.68 ± 0.17	0.41 ± 0.09	1.90 ± 0.95	2.42 ± 0.38
0	SPIRO	24.2 ± 0.21	0.85 ± 0.02	0.51 ± 0.04	10.32 ± 0.86	16.3 ± 1.86
0.33		21.9 ± 0.50	0.86 ± 0.01	0.46 ± 0.02	8.64 ± 0.55	8.40 ± 0.70
0.50		18.8 ± 1.5	0.86 ± 0.01	0.44 ± 0.05	7.04 ± 0.63	7.43 ± 0.73
0.66		16.3 ± 1.4	0.86 ± 0.01	0.44 ± 0.02	6.17 ± 0.97	5.25 ± 0.76
1.0		13.6 ± 0.5	0.84 ± 0.01	0.46 ± 0.02	5.19 ± 0.34	3.35 ± 1.42

[a] The ± values are standard deviations.