Supporting Document:

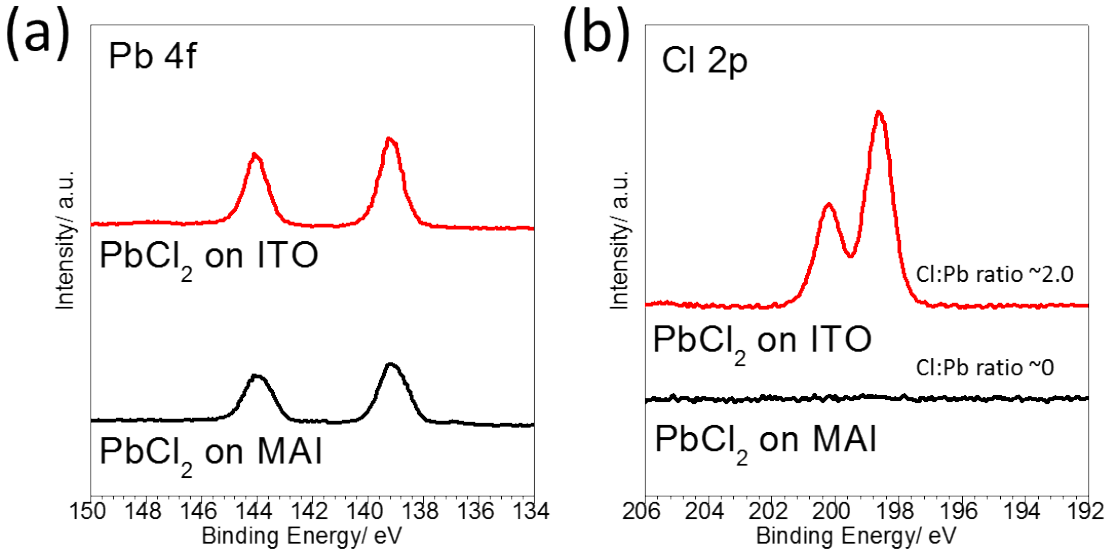

Figure S1. High resolution XPS (a) Pb 4f and (b) Cl 2p core level spectra comparing the thermal evaporated 5 nm $PbCl_2$ formed on ITO/MAI (15.0 nm) and bare ITO substrate respectively. While deposition of $PbCl_2$ on ITO is stoichiometric with Cl:Pb ratio of 2.0, the same deposition of $PbCl_2$ on ITO/MAI(15.0 nm) shows no measurable Cl content.

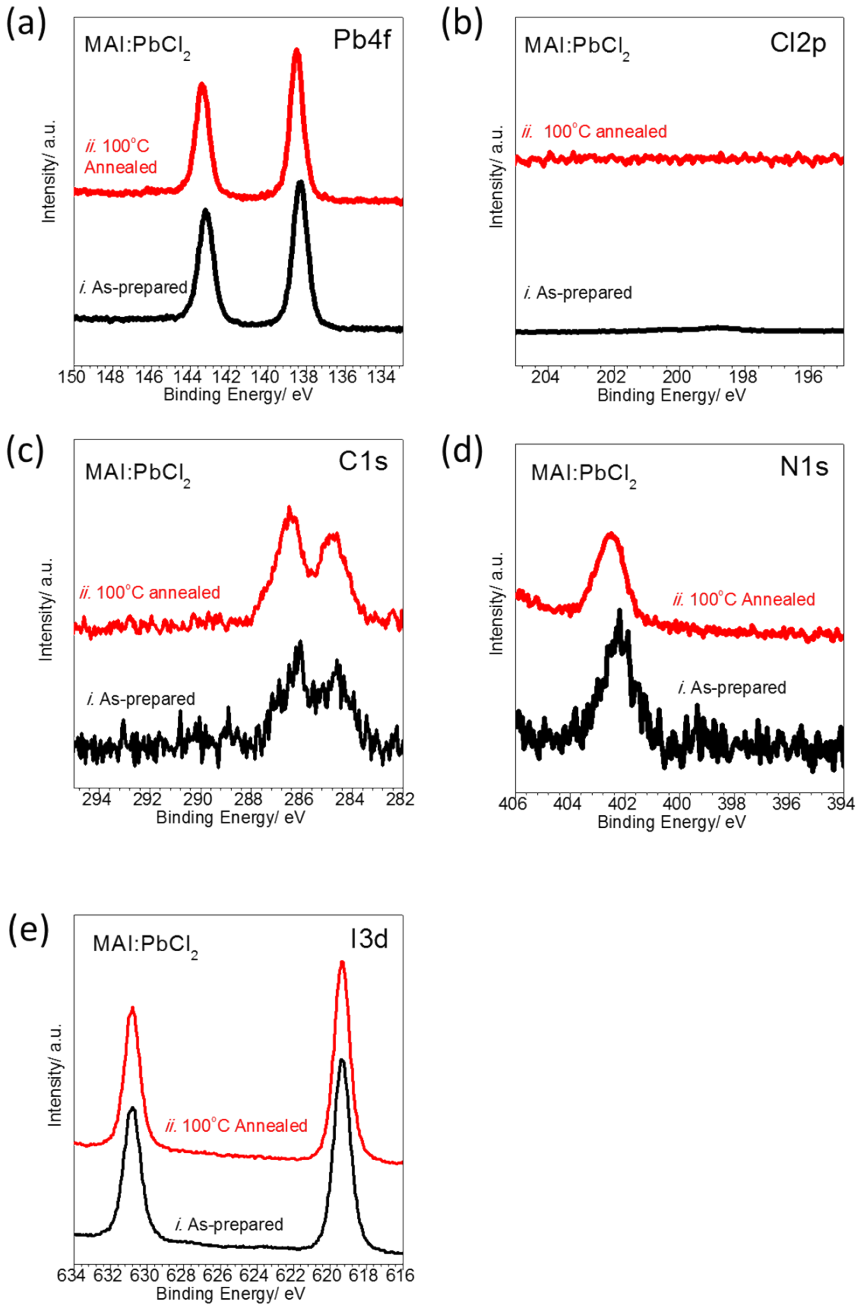

Figure S2. High resolution XPS (a) Pb 4f, (b) Cl 2p, (c) C 1s, (d) N 1s and (e) I 3d XPS core level spectra comparing the MAI:$PbCl_2$, before and after 100°C for 1 hour. No special chemical difference is observed in the testing MAI:$PbCl_2$ sample before and after 100°C annealing.

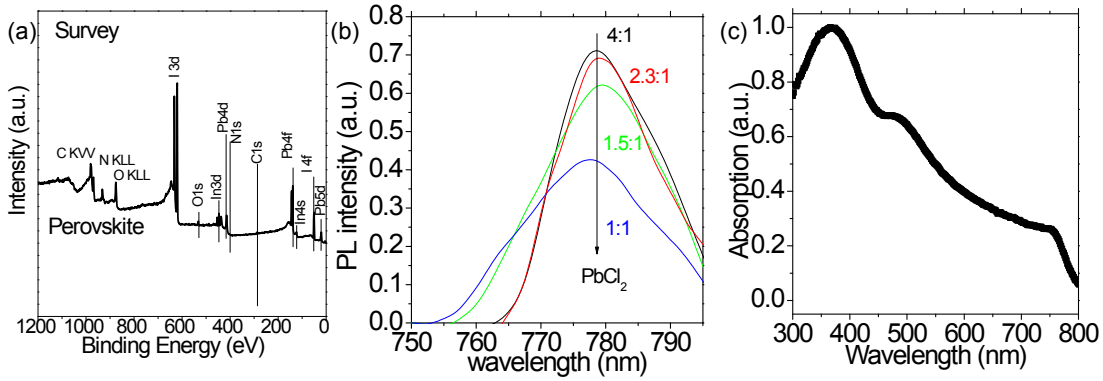

Figure S3 (a) XPS survey scan, (b) photoluminescence spectra and (c) absorption spectrum of perovskite film.

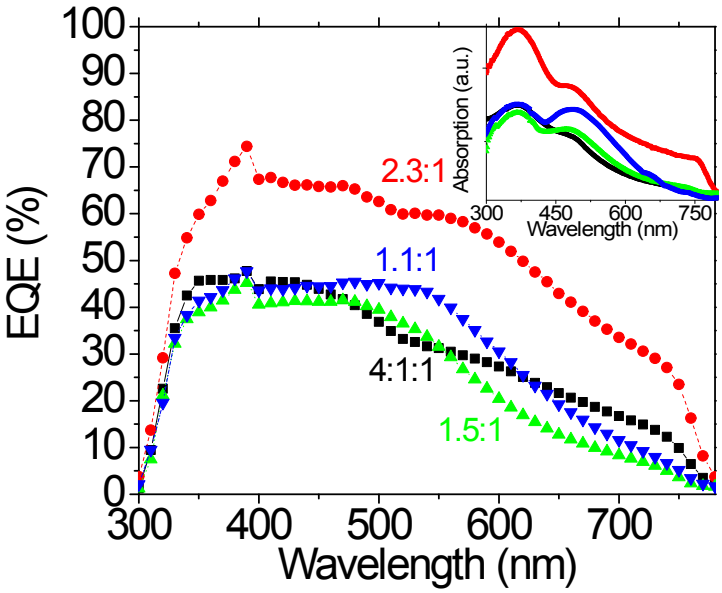

Figure S4 EQE spectra of perovskite solar cells with different MAI:$PbCl_2$ ratios. Inset shows the corresponding absorption of perovskite films.

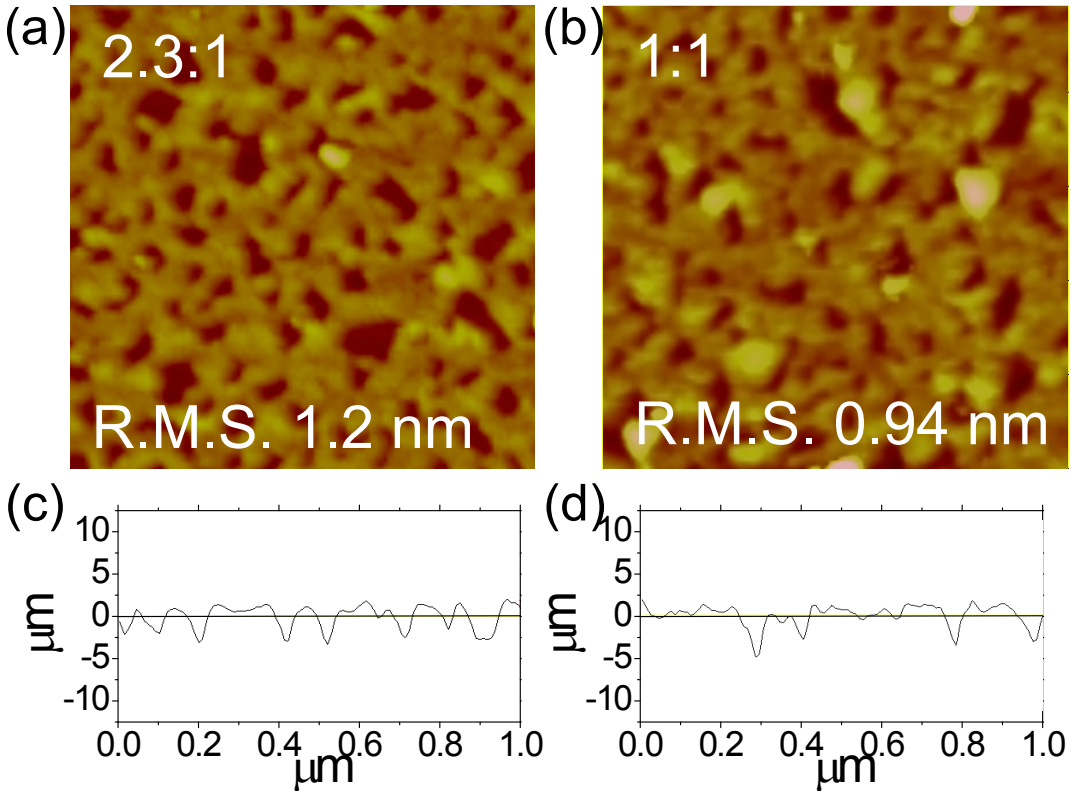

Figure S5 AFM of perovskite film with MAI:$PbCl_2$ ratios of (a) 2.3:1 and (b) 1:1. The related cross-section morphologies are shown in (c) and (d) respectively.

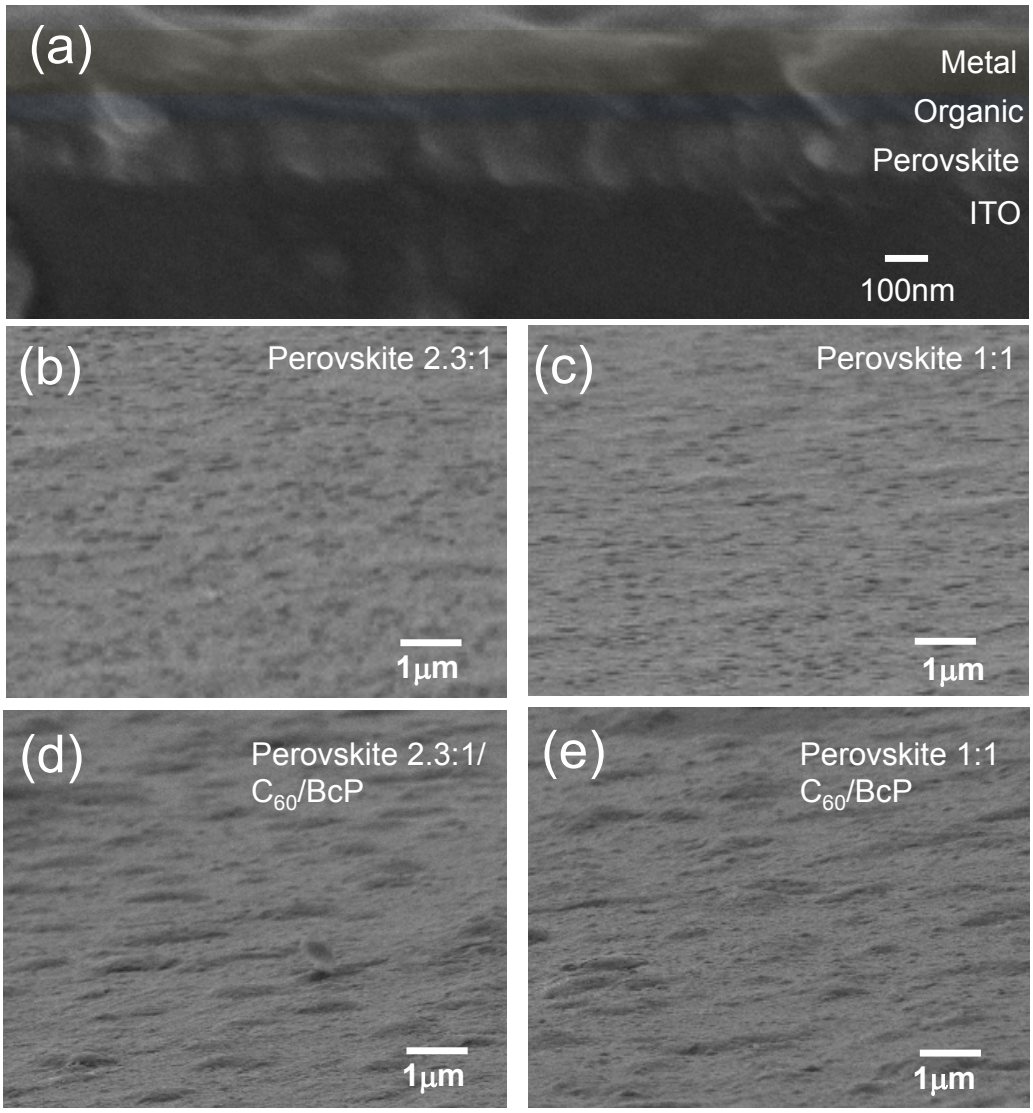

Figure S6 SEM images of (a) cross-section of the perovskite devices. Perovskite film with MAI:$PbCl_2$ ratios of (b) 2.3:1 and (c) 1:1. Film morphologies with C_{60}/BCP film deposited on perovskites with MAI:PbCl2 ratios of (d) 2.3:1 and (e) 1:1.

Experimental details:

Thermal evaporator consist of a vacuum chamber of base vacuum better than 10^{-6} Torr equipped with a vacuum pump (i.e. CTI Cryo pump) and electrically heated quartz crucibles for holding the source materials. A substrate holder is set about 10 inches about the crucibles. During sample preparation, an ITO coated glass substrate is put on the substrate holder with the ITO side facing the crucibles. CH_3NH_3I (from Lumtech.) and $PbCl_2$ (from Sigma Aldrich) are used as-received and load into two different crucibles. Evaporation temperatures for CH_3NH_3I and $PbCl_2$ are ~120 and ~ 325 °C respectively. A quartz crystal monitor is positioned close to the substrate and used for monitoring the thickness of the deposited film. Doping ratio in the film is precisely controlled with two additional crystal monitors.

Detailed operation procedure is as follows,

1. $PbCl_2$ or MAI are deposited on the Si substrates for 30 minutes at a fixed evaporation rate and the final deposited thickness can be recorded on the crystal monitor.
2. The actual deposited films thickness were characterized using ellipsometer.
3. The tooling factors were justified by comparing the system-estimated thickness and the actual measured thickness. It is noted that this factor highly depends on the mean-free-path of evaporated source and the source-to-substrate distance, this would vary system-by-system.
4. With all these deposition parameters, doping ratio of co-evaporation can be controlled.
5. Finally the doping ratio of two sources is recorded and verified with XPS.