## Supplemental Information for Enhanced self-assembled monolayer surface coverage by ALD NiO in p-i-n PSCs



**Figure 1** High-angle annular dark-field images of cross-section of (a) the ITO/MeO-2PACz device, and (b) the ITO/NiO+MeO-2PACz device.



**Figure 2** (a) Schematic of conductive atomic force microscopy (c-AFM) where the layers are biased at 100 mV and a metal-coated AFM tip is used to collect the current signal from the surface. (b) Height and current map of ITO+MeO-2PACz layer and (c) corresponding line profile along the dashed line. Similarly, (d) shows the c-AFM height and current maps of NiO+MeO-2PACz layer with line profile plotted in (e).



**Figure 3** Box charts of PV parameters of devices (ITO/(NiO/)SAM/CsFAMA/C<sub>60</sub>/BCP/Cu (CsFAMA is  $Cs_{0.05}FA_{0.92}MA_{0.03}Pb(I_{0.83}Br_{0.17})_3$  with FA as formamidinium, MA as methylammonium, and BCP is bathocuproine) using ALD NiO with post-annealing at 300°C for 20 min in air, MeO-2PACz and ALD NiO (without post-treatment)+MeO-2PACz: (a) Power conversion efficiency (PCE); (b) Open circuit voltage (V<sub>OC</sub>); (c) Fill factor (FF); (d) Short circuit current (J<sub>SC</sub>). The data are collected from reverse second J-V scan with 100 mV/s scan rate. Box charts represent 25-75%, whiskers are 5%-95%, rest is outliers. Data collected from 36 devices (active area of 0.16 cm<sup>2</sup>), with each condition reported from several different batches.