

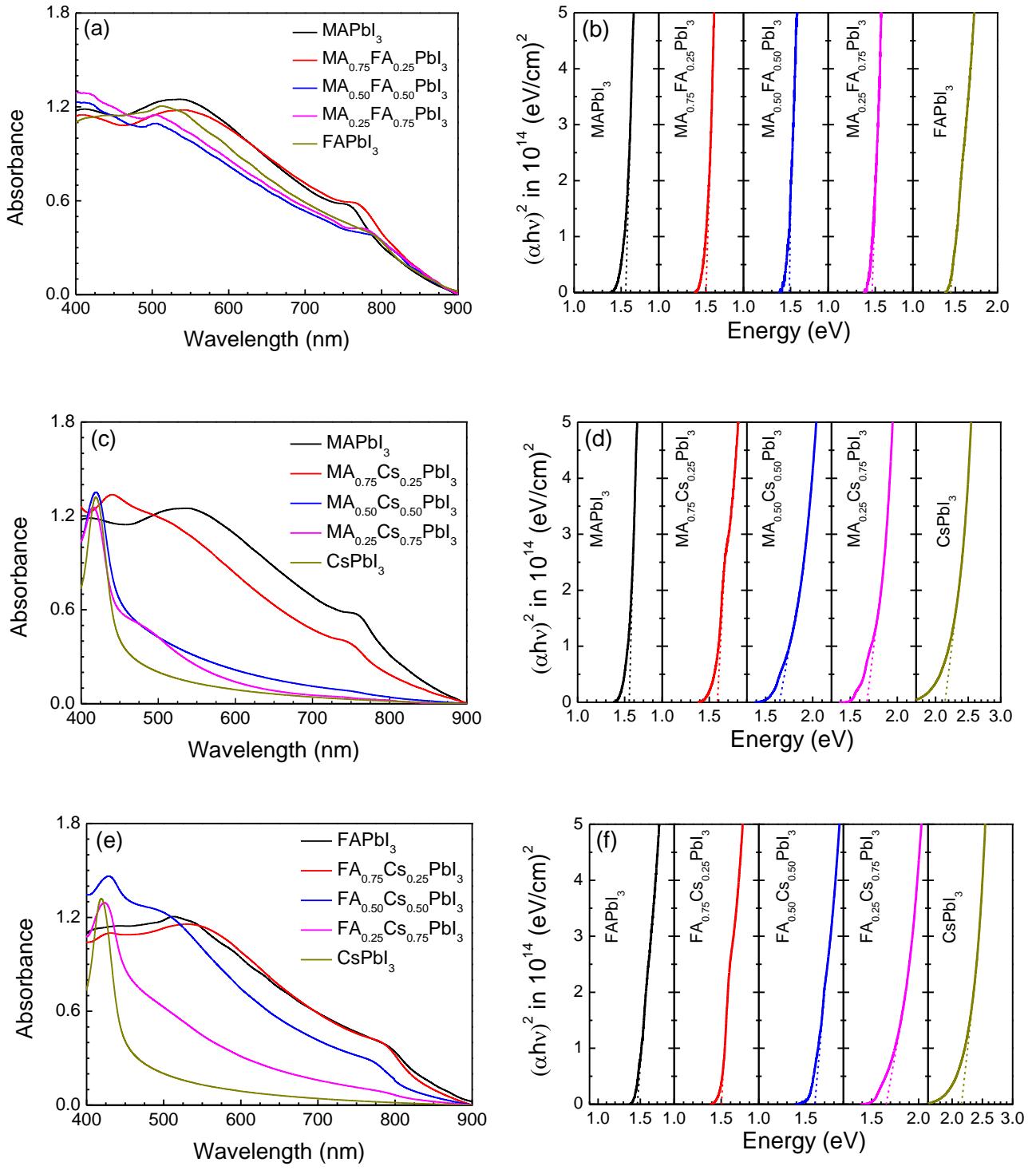
Supporting Information for

# Band-Edges of Hybrid Halide Perovskites under the Influence of Mixed Cation Approach: A Scanning Tunneling Spectroscopic Insight

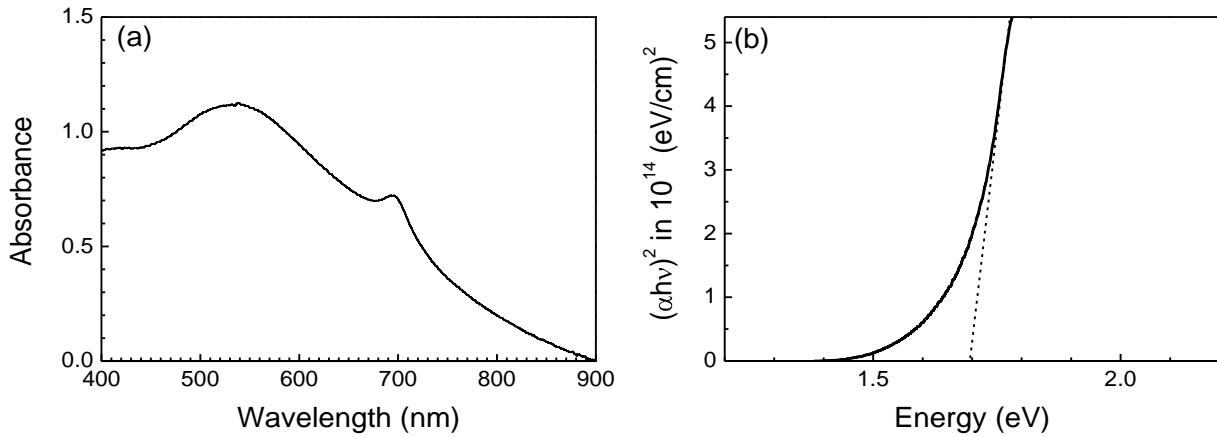
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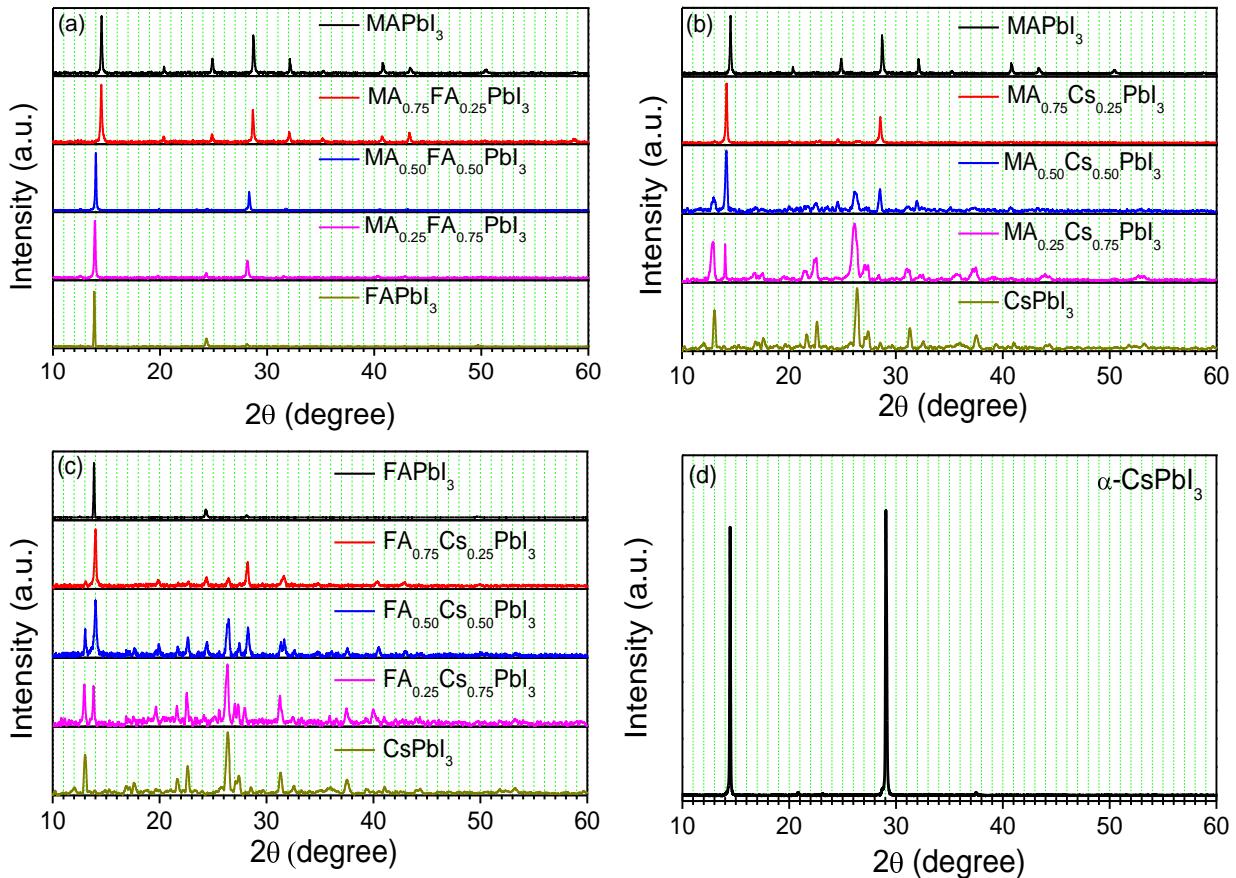
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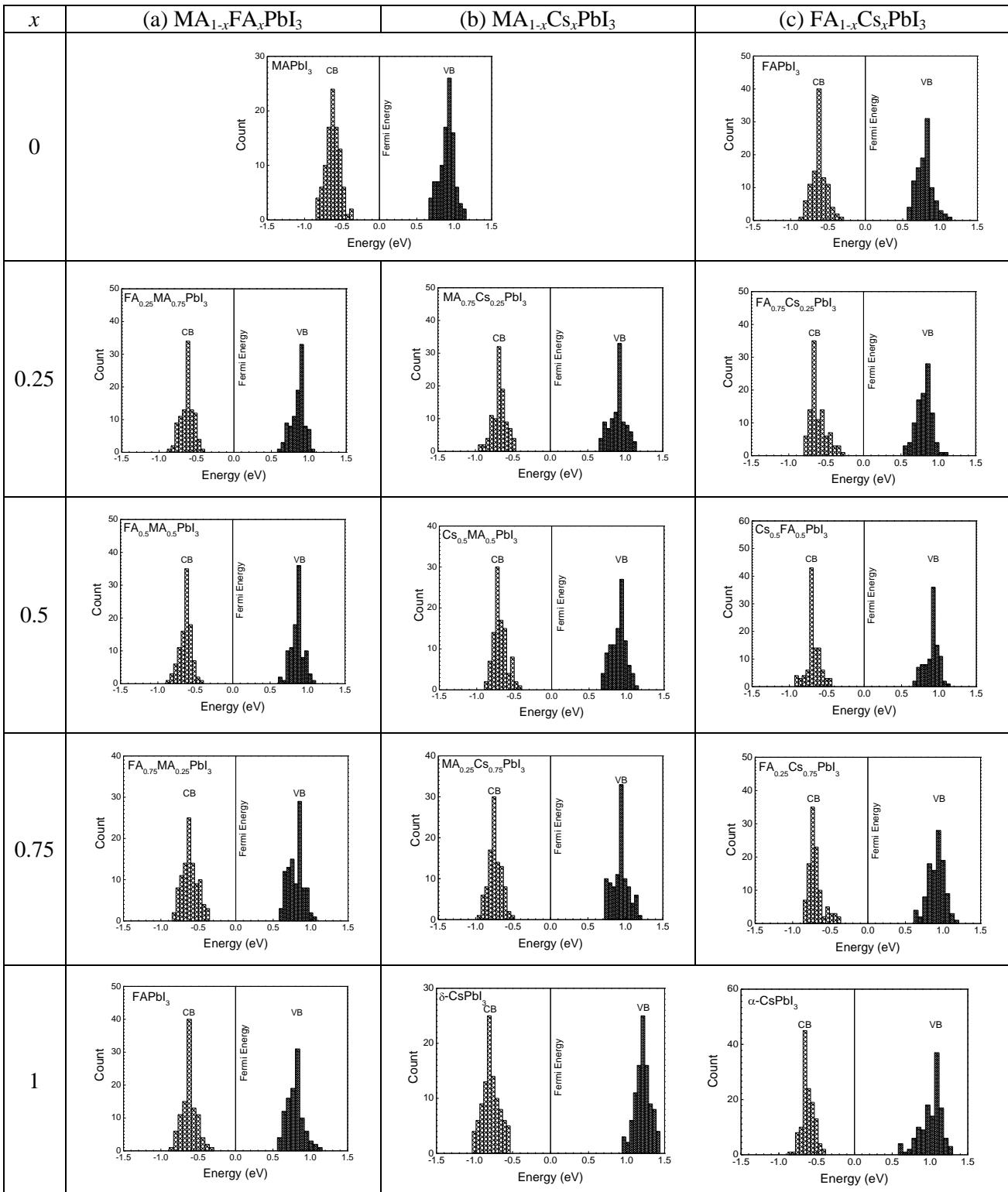
**Figure S1.** Optical absorption spectra and corresponding Tauc plots of (a and b)  $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ , (c and d)  $\text{MA}_{1-x}\text{Cs}_x\text{PbI}_3$ , and (e and f)  $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$  at different doping contents.



**Figure S2.** (a) Optical absorption spectrum and (b) corresponding Tauc plot of  $\alpha$ -CsPbI<sub>3</sub>.

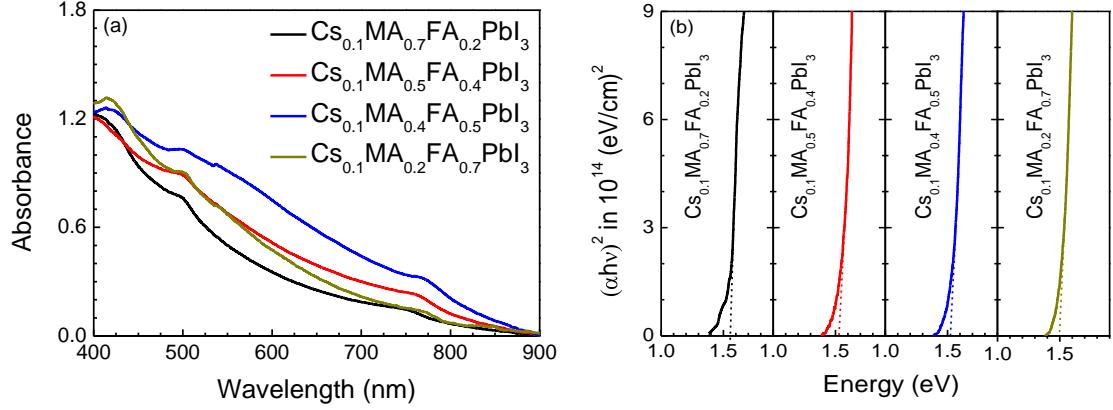


**Figure S3.** XRD patterns of (a)  $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ , (b)  $\text{MA}_{1-x}\text{Cs}_x\text{PbI}_3$ , (c)  $\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$  perovskite thin-films at different doping contents and (d)  $\alpha$ -CsPbI<sub>3</sub>.

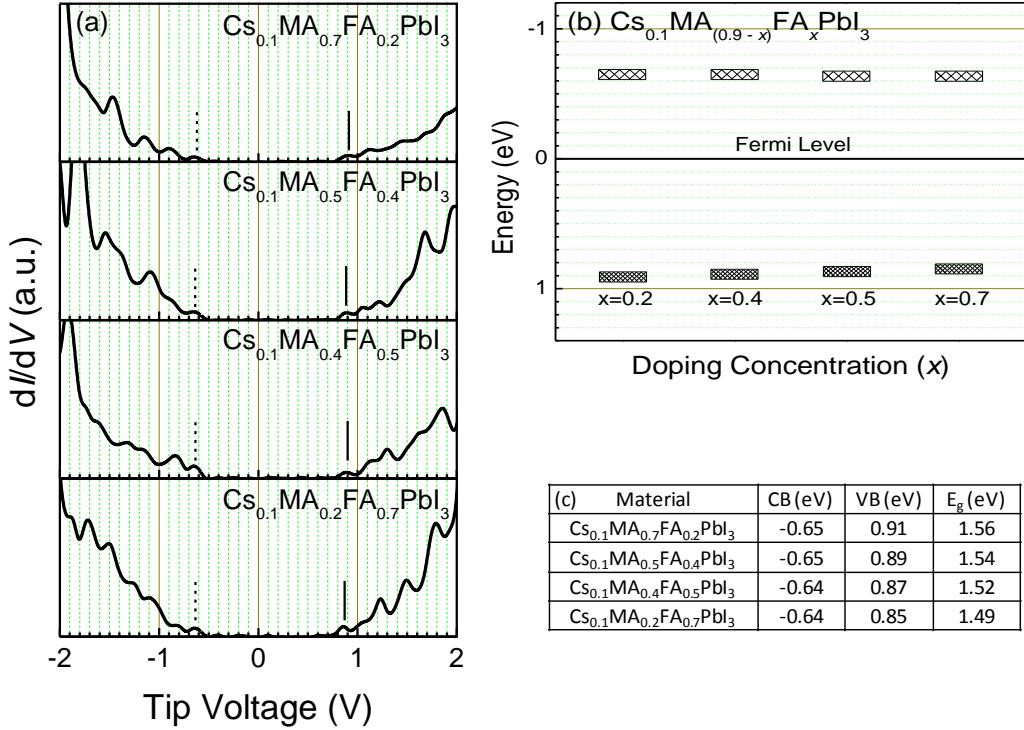


**Figure S4.** Histograms of CB and VB-edges of (a)  $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ , (b)  $\text{MA}_{1-x}\text{Cs}_x\text{PbI}_3$ , and (c)

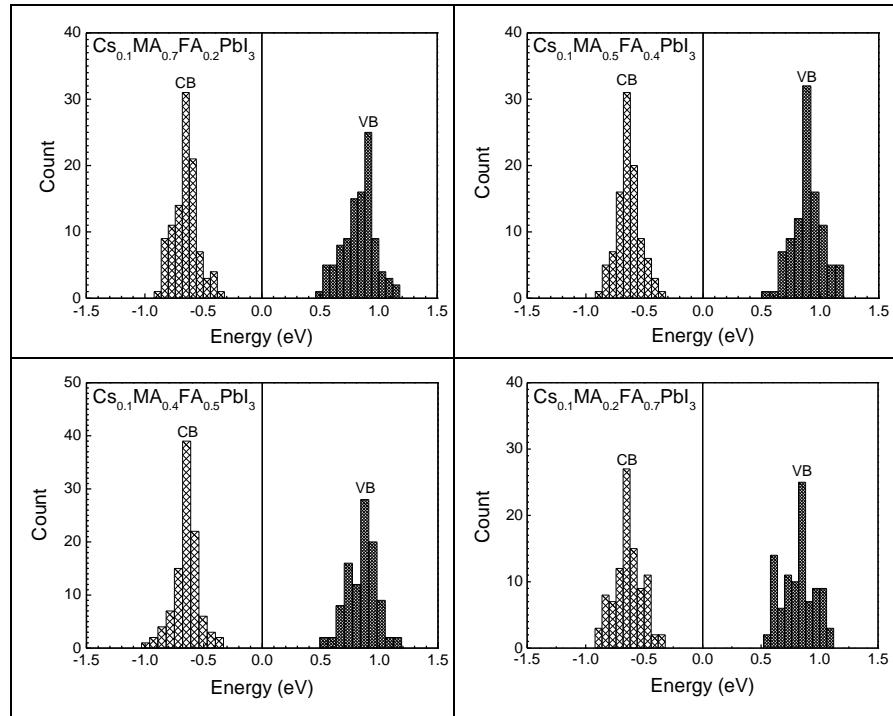
$\text{FA}_{1-x}\text{Cs}_x\text{PbI}_3$  perovskite thin-films at different doping contents. For  $\text{CsPbI}_3$ , histograms have been provided for its delta- and alpha-phases, which represent non-perovskite and perovskite structure, respectively.



**Figure S5.** (a) Optical absorption spectra and corresponding (b) Tauc plots of  $\text{Cs}_{0.1}\text{MA}_{0.9-x}\text{FA}_x\text{PbI}_3$ , ( $x = 0.2, 0.4, 0.5$  and  $0.7$ ).



**Figure S6.** (a) Typical dI/dV spectra, corresponding (b) band diagram, and (c) band energy values of  $\text{Cs}_{0.1}\text{MA}_{0.9-x}\text{FA}_x\text{PbI}_3$ , ( $x = 0.2, 0.4, 0.5$  and  $0.7$ ).



**Figure S7.** Histograms of VB and CB edges of  $\text{Cs}_{0.1}\text{MA}_{0.9-x}\text{FA}_x\text{PbI}_3$  ( $x = 0.2, 0.4, 0.5$  and  $0.7$ ).