Supporting Information

Molecular Modulator for Stable Inverted Planar Perovskite Solar Cells with Efficiency Enhanced by Interface Engineering

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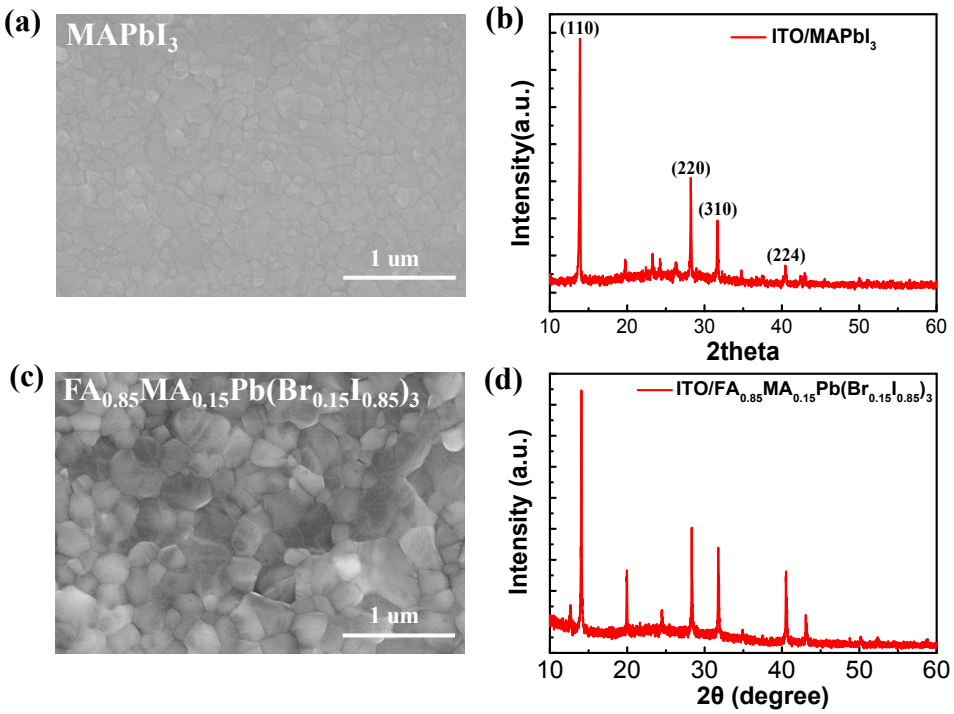

Figure S1. The surface SEM image (a) and XRD patterns (b) of $MAPbI_3$ on ITO substrate; surface SEM image(c) and XRD patterns (d) of $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$ on ITO substrate (scale bars: 1 μm).

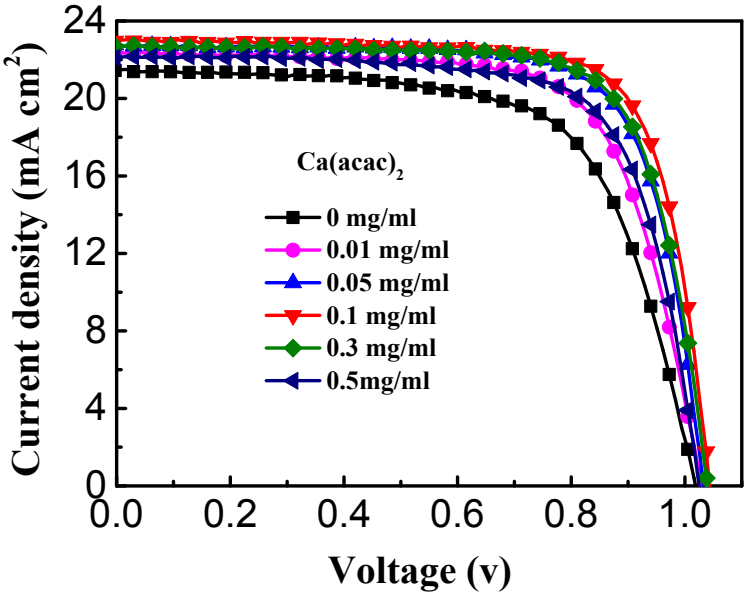

Figure S2. Typical J-V curves of perovskite solar cells with different concentration of $Ca(acac)_2$. The measurements were carried out under AM 1.5 illumination at an irradiation intensity of 100 mW·cm^{-2} ($MAPbI_3$-based PSCs)

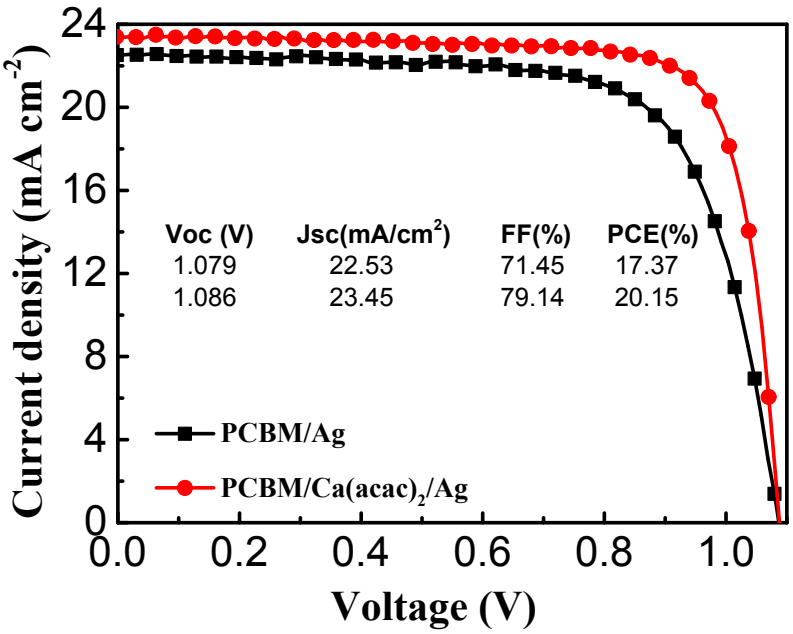

Figure S3. *J–V* curves under the AM 1.5 G simulated sunlight illumination (100 mW·cm^{-2}) for the inverted planar perovskite solar cells with and without $Ca(acac)_2$ interfacial layer ($FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$-based PSCs).

Table S1. Photovoltaic parameters of the perovskite solar cells with different $Ca(acac)_2$ concentration ($MAPbI_3$-based PSCs).

Sample	V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
0 mg/ml	1.02	21.49	66.29	14.53
0.01 mg/ml	1.03	22.37	70.19	16.17
0.05 mg/ml	1.03	22.69	74.68	17.45
0.1 mg/ml	1.04	23.02	75.95	18.23
0.3 mg/ml	1.03	22.76	74.73	17.52
0.5 mg/ml	1.02	22.13	72.91	16.46

Table S2. Photovoltaic parameters of the best PSCs without and with $Ca(acac)_2$ ETLs in different scan directions ($MAPbI_3$-based PSCs)

Scan direction	V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
PCBM/Ag (Forward)	0.98	21.11	60.03	12.42
PCBM/Ag (Reverse)	1.02	21.49	66.29	14.53
PCBM/$Ca(acac)_2$/Ag (Forward)	1.04	22.76	76.75	18.16
PCBM/$Ca(acac)_2$/Ag (Reverse)	1.04	23.02	75.95	18.23

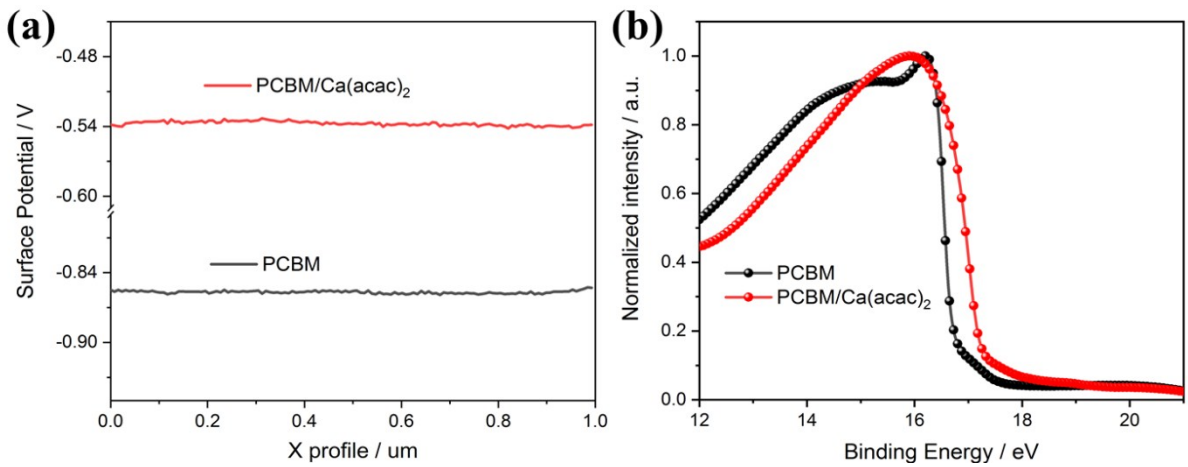

Figure S4. a) Surface potential profiles (V_{sp}) extracted from the SKPM images; b) UPS spectra of the pure PCBM and $Ca(acac)_2$ coated PCBM films. The work function of PCBM was reduced after $Ca(acac)_2$ modification.

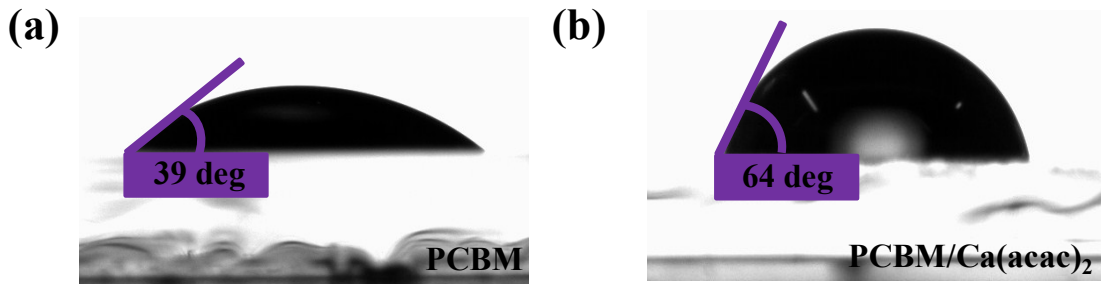

Figure S5. Contact angles of water on PCBM (a) and PCBM/$Ca(acac)_2$ (b) films.

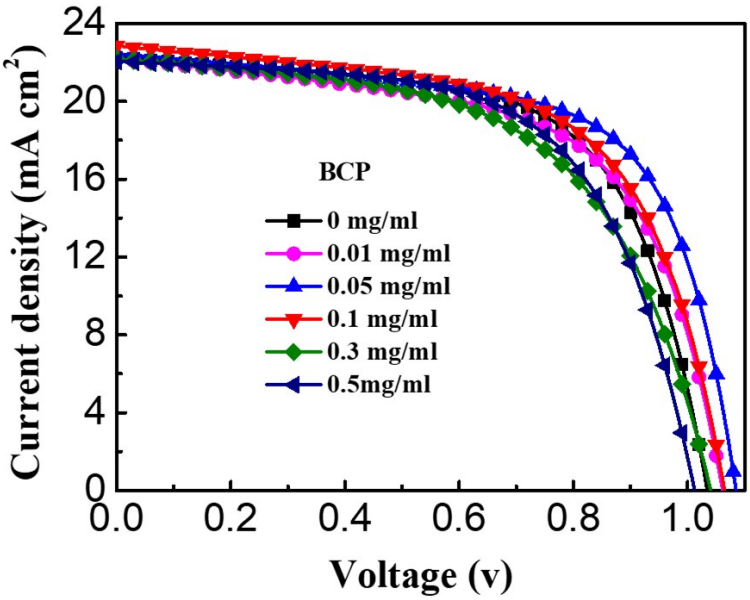

Figure S6. Typical J-V curves of perovskite solar cells with different concentration of BCP. The measurements were carried out under AM 1.5 illumination at an irradiation intensity of 100 mW•cm^{-2} ($MAPbI_3$-based PSCs)

Table S3. Photovoltaic parameters of the perovskite solar cells with different BCP concentration ($MAPbI_3$-based PSCs).

Sample	V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
0 mg/ml	1.02	22.24	62.8	14.24
0.01 mg/ml	1.05	22.20	61.2	14.26
0.05 mg/ml	1.07	22.43	63.5	15.24
0.1 mg/ml	1.06	22.84	61.1	14.79
0.3 mg/ml	1.03	22.18	56.7	12.95
0.5 mg/ml	0. 997	22.05	61.2	13.45

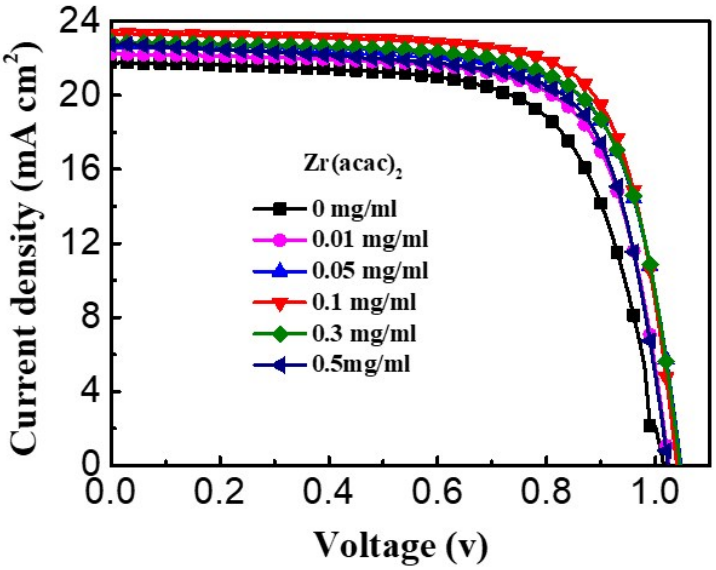

Figure S7. Typical J-V curves of perovskite solar cells with different concentration of $Zr(acac)_2$. The measurements were carried out under AM 1.5 illumination at an irradiation intensity of 100 mW•cm^{-2} ($MAPbI_3$-based PSCs)

Table S4. Photovoltaic parameters of the perovskite solar cells with different $Zr(acac)_2$ concentration ($MAPbI_3$-based PSCs).

Sample	V_{oc} (V)	J_{sc} (mA·cm^{-2})	FF (%)	PCE (%)
0 mg/ml	1.027	21.75	68.40	15.27
0.01 mg/ml	1.033	22.24	71.80	16.49
0.05 mg/ml	1.038	22.78	72.20	17.07
0.1 mg/ml	1.040	23.32	74.10	17.97
0.3 mg/ml	1.040	22.89	72.31	17.21
0.5 mg/ml	1.025	22.74	72.36	16.86

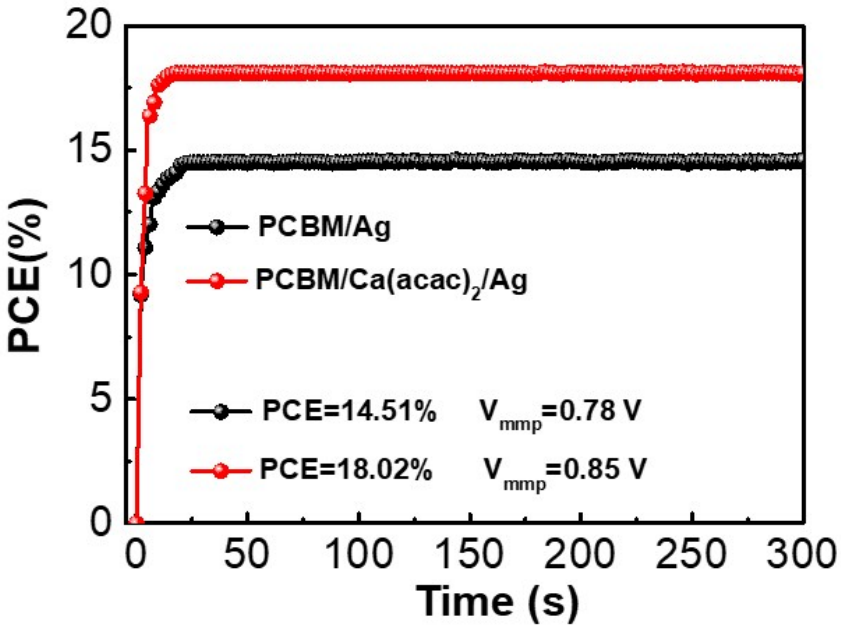

Figure S8. Steady photocurrent and PCE output at a fixed bias voltage of its initial maximal power point of each champion device ($MAPbI_3$-based PSCs).

The steady-state power output for the control and also for the best device with $Ca(acac)_2$ as cathode interfacial layers (CILs). The voltage for the devices without and with $Ca(acac)_2$ are 0.78 V and 0.85 V, respectively, the maximum current density are 18.60 mA/cm^2 and 21.2 mA/cm^2, respectively, and the steady-state output are 14.51 % and 18.02% for control and $Ca(acac)_2$ as CILs devices, respectively.

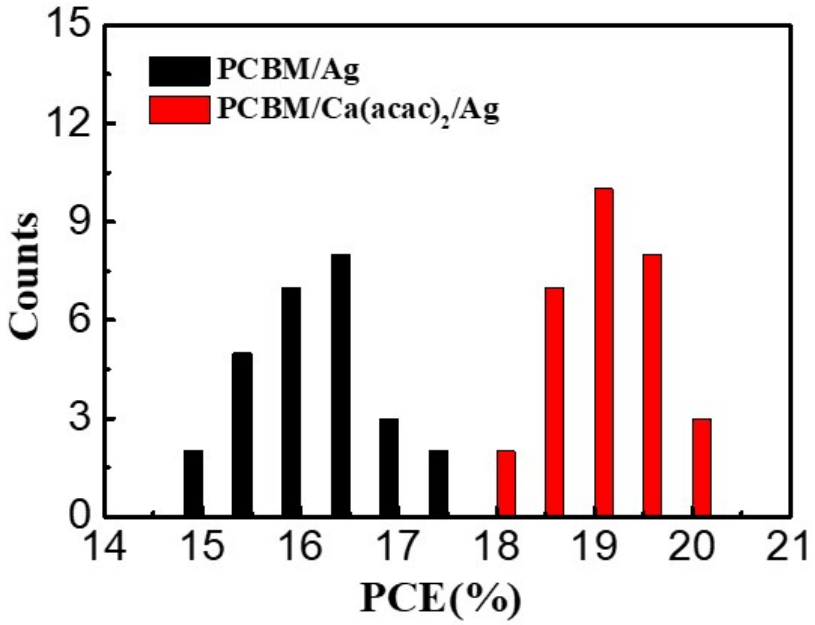

Figure S9. For $FA_{0.85}MA_{0.15}Pb(I_{0.85}Br_{0.15})_3$.-based PSC devices: Histogram of solar cell efficiencies of the control and $Ca(acac)_2$-modified PSCs (30 devices, respectively).