Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary Information for

Synergistic Passivation of Perovskite Surfaces Using a Multi-Functional Four-End Zwitterionic Amino Acid

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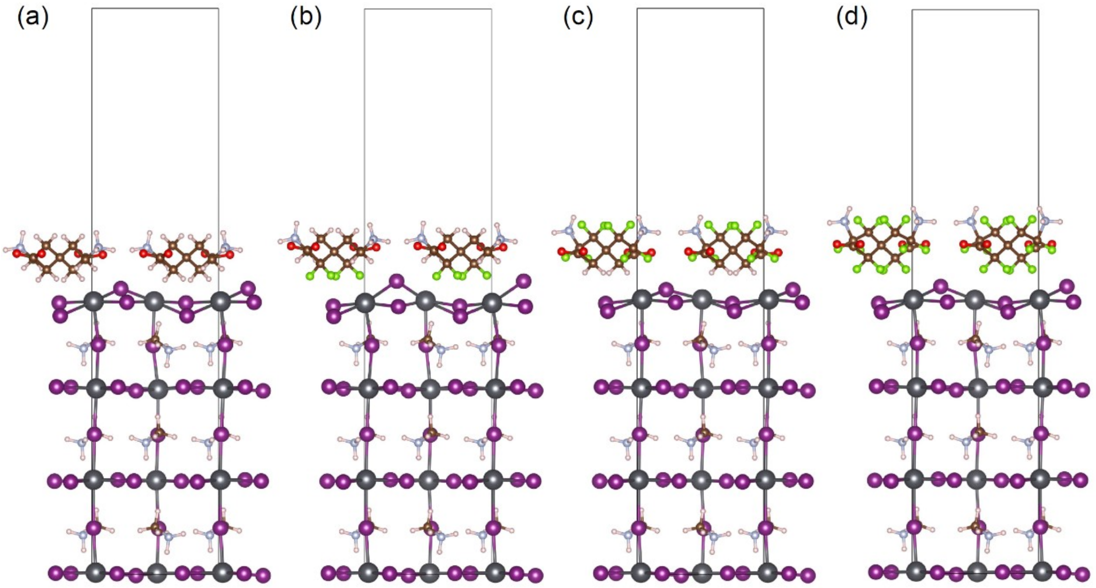

Figure S1 The structures (a) $\mathrm{ZAA_{allH}}$-PS-mode2, (b) $\mathrm{ZAA_{CF}}$-PS-mode2, (c) $\mathrm{ZAA_{NF}}$-PS-mode2, and (d) $\mathrm{ZAA_{allF}}$-PS-mode2.

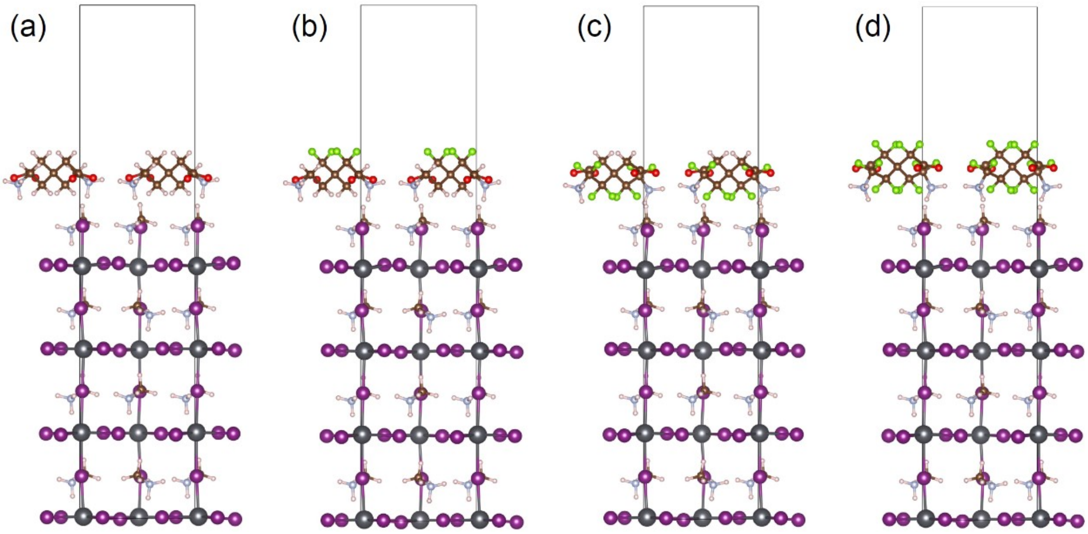

Figure S2 The optimized structures of (a) ZAA$_{\mathrm{allH}}$, (b) ZAA$_{\mathrm{CF}}$, (c) ZAA$_{\mathrm{NF}}$, and (d) ZAA$_{\mathrm{allF}}$ on the perovskite with MAI-terminated surface.

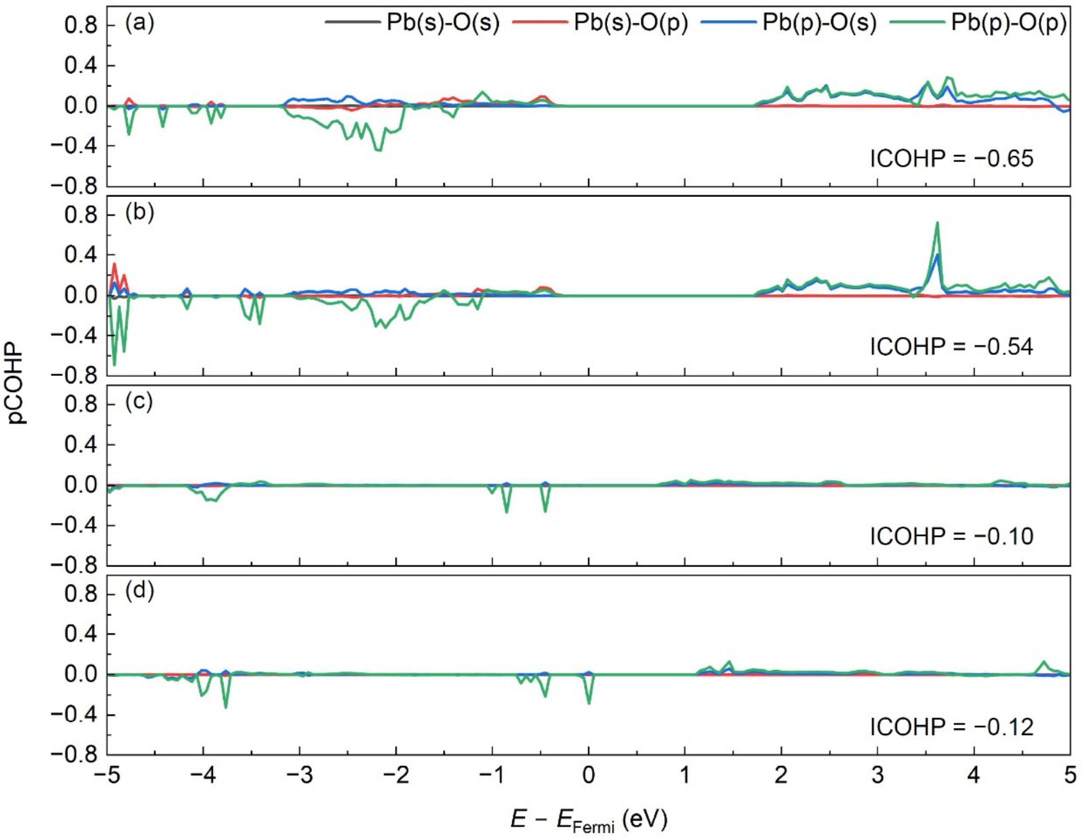

Figure S3 The average pCOHP between O and Pb in (a) ZAA_{allH}-PS, (b) ZAA_{CF}-PS, (c) ZAA_{NF}-PS, and (d) ZAA_{allF}-PS. The ICOHP is labeled at the bottom right corner.

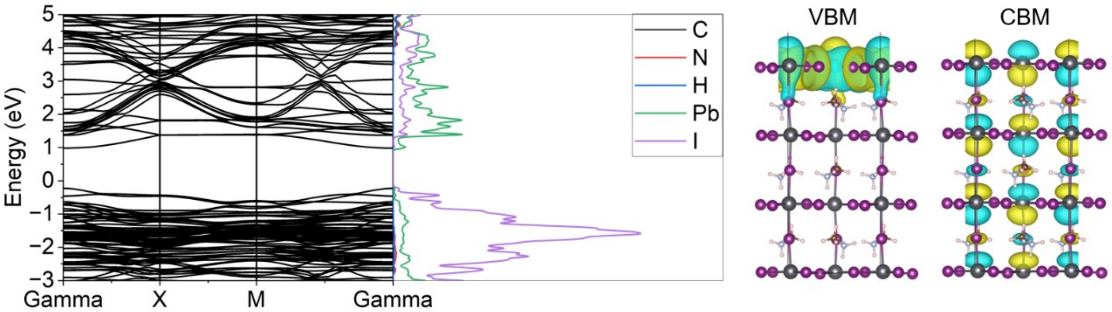

Figure S4 The band structure and projected density of states (PDOS), and the real-space distribution of the wave function of VBM and CBM with an isosurface value of 2×10^{-8} e/bohr^3 of the PS.

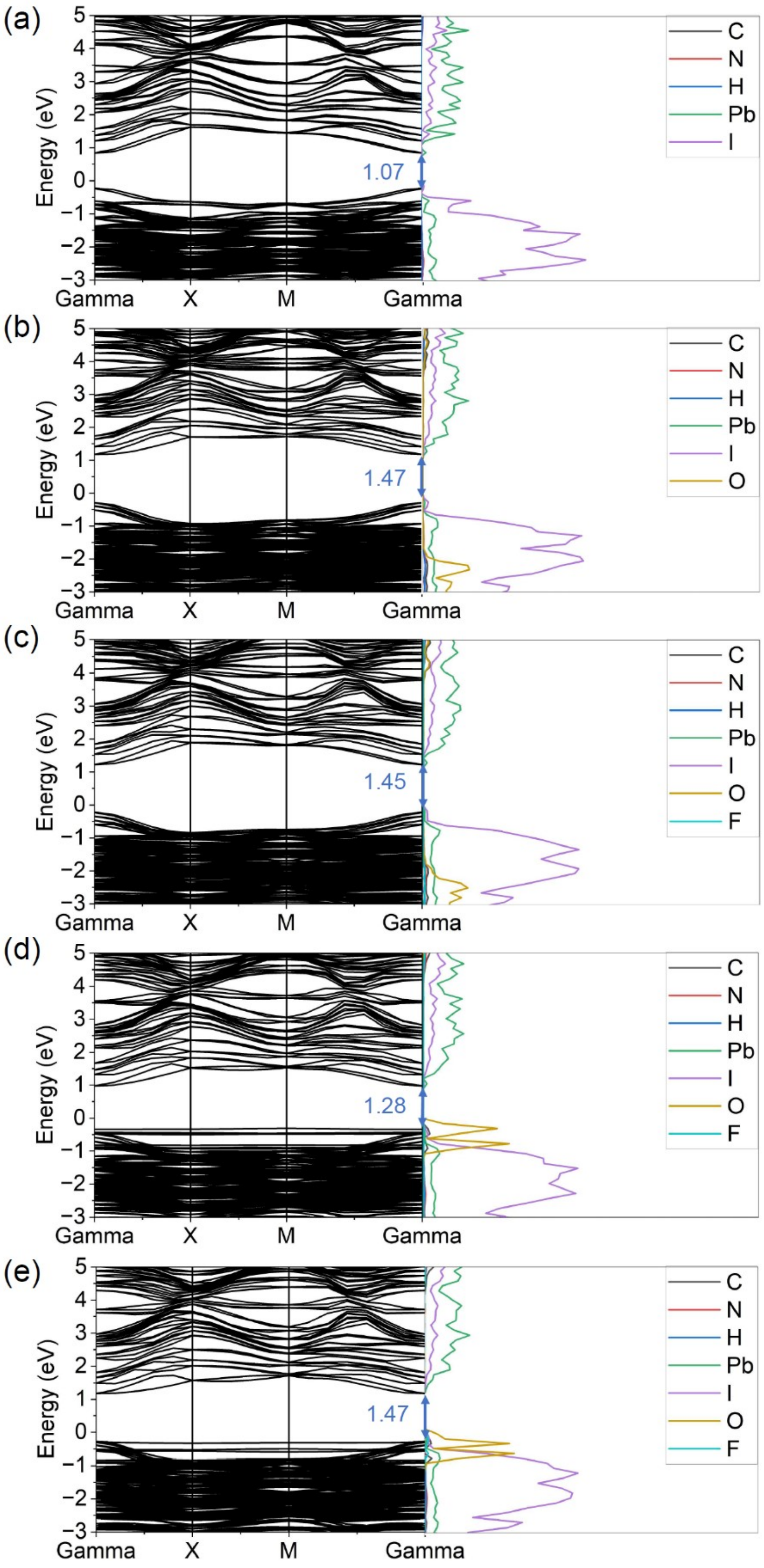

Figure S5 The band structure and projected density of states (PDOS) calculated by HSE+SOC of (a) PS, (b) ZAA$_{\mathrm{allH}}$-PS, (c) ZAA$_{\mathrm{CF}}$-PS, (d) ZAA$_{\mathrm{NF}}$-PS, and (e) ZAA$_{\mathrm{allF}}$-PS, respectively.

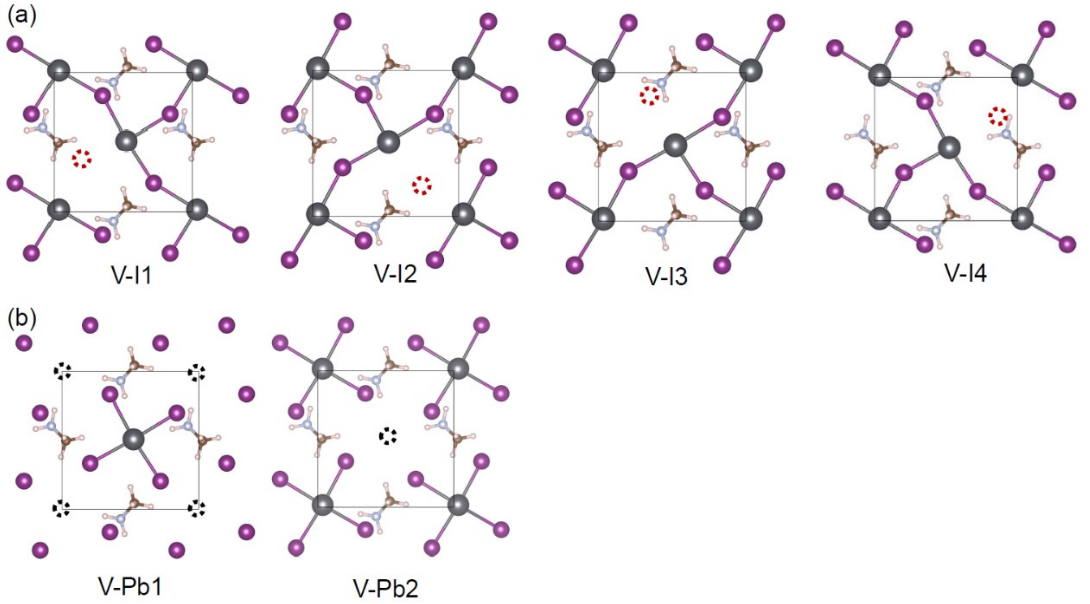

Figure S6 The locations of the various defect sites of (a) the I vacancy indicated by a red dashed line, and (b) the Pb vacancy indicated by a black dashed line.

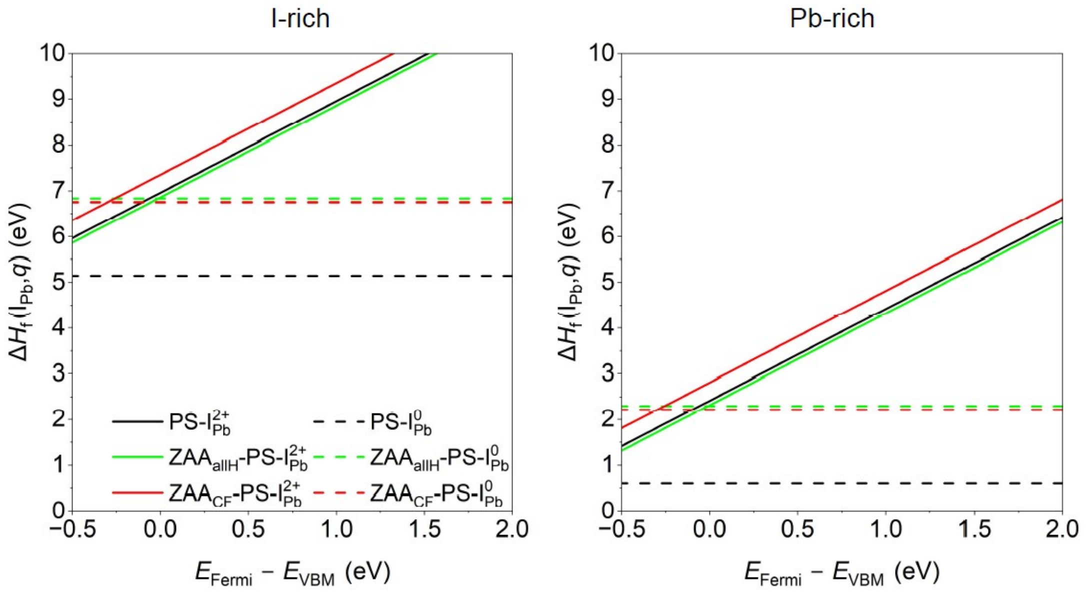

Figure S7 The formation energies of Pb interstitial defects ($\Delta H_f(I_{Pb},q)$) in PS, ZAA$_{allH}$-PS, and ZAA$_{CF}$-PS at I-rich (left) and Pb-rich (right) chemical potentials.

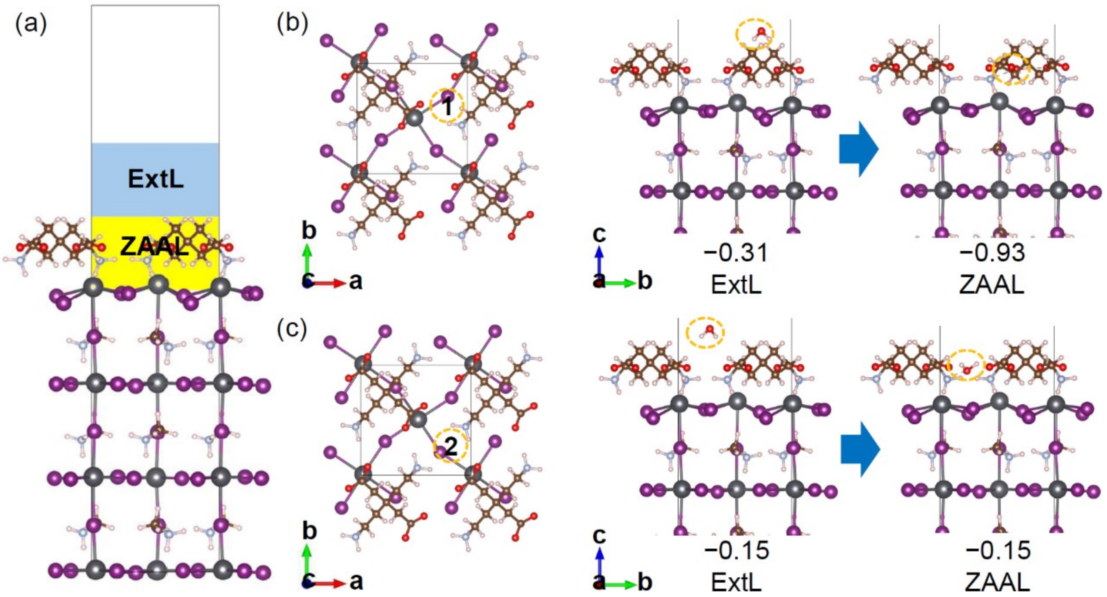

Figure S8 (a) Two zones in the shallow surface of ZAA_{allH}-PS for H_2O invasion, labelled as ExtL and ZAAL from outside to inside the surface. The invasion process of H_2O from (b) site 1 and (c) site 2, with the relative energy ($E_{r\text{-}H2O}$) in eV. The H_2O is indicated by an orange dashed line.

Table S1 The Pb…O distances between oxygen atoms in ZAA and Pb atoms on the surface of the perovskite (d_1'-d_4', Å), average Pb…O distance ($\bar{d}'$, Å). Binding energy between ZAA and perovskite of mode2 (E_b', eV). Binding energy difference between E_b' and E_b (eV).

	d_1'	d_2'	d_3'	d_4'	$\bar{d}'$	E_b'	$E_b' - E_b$
ZAA$_{\text{allH}}$-PS-mode2	3.33	3.46	3.46	3.51	3.44	2.99	−2.05
ZAA$_{\text{CF}}$-PS-mode2	3.86	3.92	3.97	3.98	3.93	2.15	−2.4
ZAA$_{\text{NF}}$-PS-mode2	3.29	3.37	3.47	3.52	3.41	2.87	−1.19
ZAA$_{\text{allF}}$-PS-mode2	3.95	3.96	4.00	4.06	3.99	1.40	−1.87

Table S2 Binding energy between ZAA and perovskite with PbI-terminated surface (E_b, eV), and binding energy between ZAA and perovskite with MAI-terminated surface (E_b-other, eV)

	E_b	E_b-other
ZAA$_{\text{allH}}$-PS	5.04	3.69
ZAA$_{\text{CF}}$-PS	4.55	2.86
ZAA$_{\text{NF}}$-PS	4.06	2.87
ZAA$_{\text{allF}}$-PS	3.27	1.94

Table S3 The band gaps (eV) of PS, ZAA$_{\text{allH}}$-PS, ZAA$_{\text{CF}}$-PS, ZAA$_{\text{NF}}$-PS, and ZAA$_{\text{allF}}$-PS calculated by different methods.

	PBE	PBE+SOC	HSE+SOC
PS	1.21	0.40	1.07
ZAA$_{\text{allH}}$-PS	1.71	0.90	1.47
ZAA$_{\text{CF}}$-PS	1.70	0.91	1.45
ZAA$_{\text{NF}}$-PS	0.78	0.28	1.28
ZAA$_{\text{allF}}$-PS	1.10	0.56	1.47

Defect formation energy calculations

The defect formation energy $\Delta H_f(\alpha,q)$ is a function of both the electron Fermi energy E_F and the chemical potentials of the species involved in the defects. It could be calculated as:

$$\Delta H_f(\alpha,q) = E(\alpha,q) - E(\text{perfect}) + \Delta n_{Pb}(E_{Pb}+\mu_{Pb}) + \Delta n_I(\frac{1}{2}E_I+\mu_I) + q(E_F + E_{VBM}) \quad \text{(S-1)}$$

where $E(\alpha,q)$ indicates the total energy calculated from the supercell with defect α in the charge state q and E(perfect) is the total energy of the supercell without any defects. Δn is the number of atoms added ($\Delta n < 0$) or removed ($\Delta n > 0$) from the supercell. μ_I, μ_{Pb}, and μ_{MA} are the chemical potential of I, Pb, and MA, respectively. The chemical potential values can be determined from the phase diagram of the MAPbI$_3$ perovskite. To obtain the phase diagram for MAPbI$_3$, the following chemical equations are considered.

$$\text{MA(s)} + \text{Pb(s)} + \frac{3}{2}\,\text{I}_2\text{(g)} \rightarrow \text{MAPbI}_3\text{(s)} \quad \text{(S-2)}$$

$$\text{MA(s)} + \frac{1}{2}\,\text{I}_2\text{(g)} \rightarrow \text{MAI(s)} \quad \text{(S-3)}$$

$$\text{Pb(s)} + \text{I}_2\text{(g)} \rightarrow \text{PbI}_2\text{(s)} \quad \text{(S-4)}$$

The ΔH_1, ΔH_2, and ΔH_3 are defined as the change in enthalpy corresponding to the reactions. The total energy of each chemical species, as summarized in Table S4. Hence, $\Delta H_1 = -8.69$ eV, $\Delta H_2 = -5.77$ eV, and $\Delta H_3 = -4.54$ eV. Assuming equilibrium among MAI, PbI$_2$, and MAPbI$_3$, μ_I, μ_{Pb}, and μ_{MA} must satisfy

$$\mu_{MA} + \mu_{Pb} + 3\mu_I = \Delta H_1 \quad \text{(S-5)}$$

$$\mu_{MA} + \mu_I < \Delta H_2 \quad \text{(S-6)}$$

$$\mu_{Pb} + 2\mu_I < \Delta H_3 \quad \text{(S-7)}$$

$$\mu_{MA}, \mu_{Pb}, \mu_{I} < 0 \tag{S-8}$$

As the I-rich condition, $\mu_I = 0$ eV, $\mu_{Pb} = -4.54$ eV, and $\mu_{MA} = -4.42$ eV. As the Pb-rich condition, $\mu_I = -2.27$ eV, $\mu_{Pb} = 0$ eV, and $\mu_{MA} = -1.88$ eV.

Table S4 Total energy (eV) of the chemical species.

Species	Total energy (eV)
I_2(g)	-2.71
Pb(s)	-3.57
MA(s)	-35.84
MAI(s)	-42.96
PbI_2(s)	-9.46
$MAPBI_3$(s)	-52.34

Simulation of Power conversion efficiency (PCE)

To get the parameters of the ZAA$_{CF}$-PS, we took them as 2D materials and did the following calculations. The effective conduction band density (N_c) and effective valence band density (N_v) are defined as

$$N_c = \frac{2(2\pi m_n^* k_0 T)^{3/2}}{h^3} \tag{S-9}$$

$$N_v = \frac{2(2\pi m_p^* k_0 T)^{3/2}}{h^3} \tag{S-10}$$

where h is Planck's constant, T is the temperature, m_n^* and m_p^* are the effective masses of electrons and holes

$$m_{n/p}^* = \frac{h}{2\pi} / \left[\frac{\partial^2 E_{VBM/CBM}}{\partial k^2} \right] \tag{S-11}$$

where E is the total energy of the system.

According to the deformation potential theory,[1] the carrier mobility (μ) of 2D materials can be calculated according to the equation[2]

$$\mu = \frac{2eh^3 C}{3(2\pi)^3 k_B T (m^*)^2 (E_1)^2} \tag{S-12}$$

where e is the electron charge, C is the elastic constant, and E_1 is deformation potential constant. The C and E_1 can be obtained by

$$C = \left[\frac{\partial^2 E}{\partial (\frac{\Delta a}{a_0})^2} \right] / S_0 \tag{S-13}$$

$$E_1 = \frac{\partial E_{edge}}{\partial (\frac{\Delta a}{a_0})} \tag{S-14}$$

where E_{edge} is the energy of the band edge, Δa is the change of lattice parameter relative to the equilibrium lattice parameter, and S_0 is the area of the unit cell at equilibrium.

References for the ESI

1 J. Bardeen and W. Shockley, Phys. Rev., 1950, 80, 72.

2 N. Wang, M. Li, H. Xiao, H. Gong, Z. Liu, X. Zu and L. Qiao, Phys. Chem. Chem. Phys., 2019, 21, 15097.