Supplementary Information

The orientation design of high-polarity ligand dipole CF_3-PEA for enhancing surface stability and optoelectronic properties of $FAPbI_3$ perovskite

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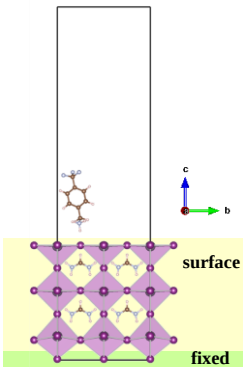

Fig. S1. The crystal structure of $FAPbI_3$ perovskite adsorbed by CF_3-PEA.

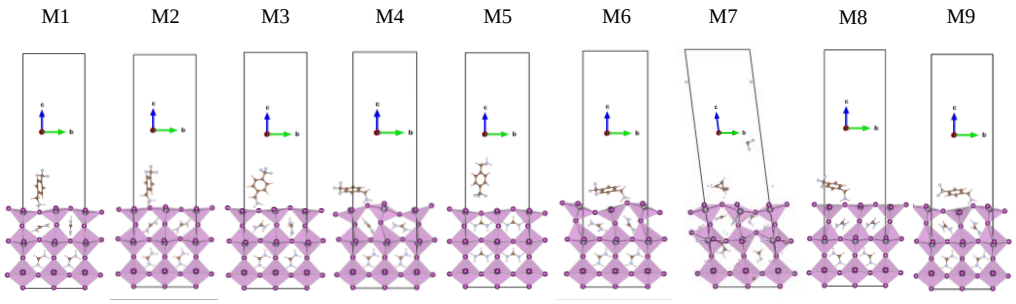

Fig. S2. The front view of atomic structure of surface adsorption systems M1-M9 after structural optimization.

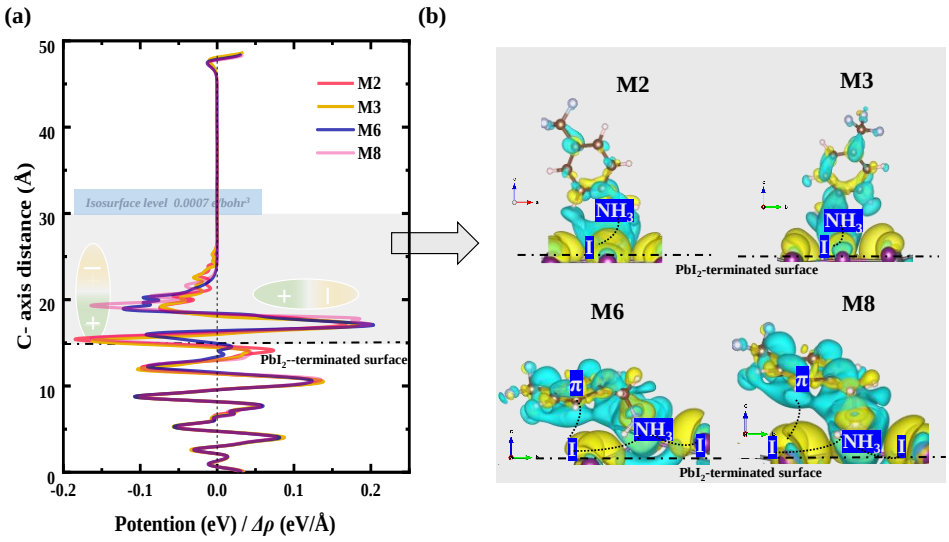

Fig. S3. (a) C-axis potential distribution and (b) Charge density difference (isosurface value of 0.0007 e/bohr^3; blue indicates electron depletion; yellow indicates electron accumulation) for systems M2, M3, M6, and M8.

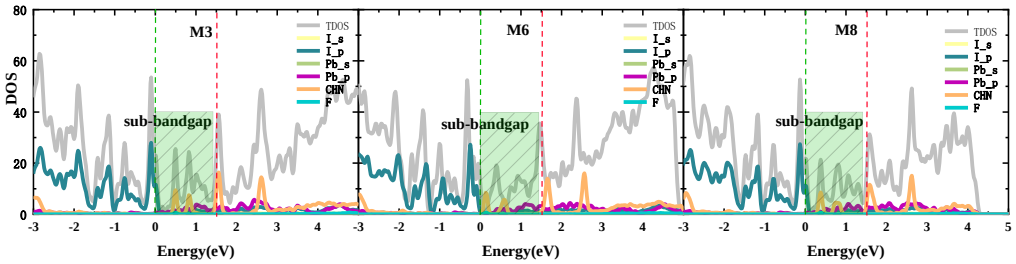

Fig. S4. Density of state of systems containing M3, M6, and M8, where VBM is corrected to be 0 eV.

Table S1. Adsorption Position with Adsorption Site and the corresponding Crystal Plane of adsorption systems M1-M6, and M8-M9.

	Adsorption Position Description	Adsorption Site	Crystal Plane
M1	Vertical adsorption of positive dipole; -NH_3 group located above C_3	C_3	[1, -1, -2]
M2	Vertical adsorption of positive dipole; -NH_3 group located above C_3	C_3	[2, -1, -4]
M3	Vertical adsorption of positive dipole; -NH_3 group located above C_3	C_3	[-2, -1, -5]
M4	Parallel adsorption of dipole; -NH_3 group located above C_3; -CF_3 group is further from the $FAPbI_3$ surface, directly above the A_2	C_3	[2, 4, -1]
M5	Vertical adsorption of negative dipole; -CF_3 group located above A_2	A_2	[0, 0, 1]
M6	Parallel adsorption of dipole; -NH3 group located above C_3; -CF_3 group is further from the $FAPbI_3$ surface, directly above the A_2	C_3	[2, 4, 1]
M8	Parallel adsorption of dipole; -NH_3 group located above C_3; -CF_3 group is further from the $FAPbI_3$ surface, directly above the A_2	C_3	[1, 1, -3]
M9	Parallel adsorption of dipole; -NH_3 group located above C_3; -CF_3 group is further from the $FAPbI_3$ surface, directly above the A_2	C_3	[1, 3, -1]

Table S2. The values of E_{tot}, ΔE_{tot}, E_{ad}, and E_{form} of Bare-$FAPbI_3$ and surface adsorption systems M1-M6, and M8-M9, respectively.

	E_{tot} (eV)	ΔE_{tot} (eV)	E_{ad} (eV)	E_{form} (eV)
Bare-$FAPbI_3$	-244.57	128.01	-	-0.485
M1	-372.42	0.16	-4.03	-0.743
M2	-372.33	0.25	-3.88	-0.740
M3	-372.36	0.22	-3.85	-0.742
M4	-372.58	0	-4.14	-0.746
M5	-369.05	3.53	-0.42	-0.477
M6	-372.52	0.06	-4.08	-0.740
M8	-372.33	0.25	-4.08	-0.728
M9	-372.50	0.08	-4.06	-0.740

Table S3. Minimum potential gradient ($\Delta\rho_{Min}$), maximum potential gradient ($\Delta\rho_{Max}$), and the resulting potential gradient span ($\Delta G = \Delta\rho_{Max} - \Delta\rho_{Min}$) along the c-axis direction for systems M1-M6, and M8-M9.

	$\Delta\rho_{Min}$ (eV/Å)	$\Delta\rho_{Max}$ (eV/Å)	ΔG (eV/Å)
M1	-0.124	0.136	0.260
M2	-0.124	0.164	0.288
M3	-0.163	0.184	0.347
M4	-0.129	0.201	0.330
M5	-0.044	0.099	0.143
M6	-0.123	0.204	0.327
M8	-0.169	0.199	0.368
M9	-0.103	0.209	0.312

Table S4. Work function (WF), Fermi level, vacuum level, and ΔWF for both the bare FAPbI3 and the adsorption systems M1-M6 and M8-M9. $\Delta WF = WF_{\text{bare FAPbI3}} - WF_{\text{system}}$.

	WF (eV)	Fermi Level (eV)	Vacuum Level (eV)	ΔWF (eV)
Bare FAPbI3	6.764	-3.505	3.259	0
M1	6.762	-1.636	5.126	0.002
M2	6.731	-1.818	4.913	0.033
M3	6.739	-1.833	4.906	0.025
M4	6.743	-1.425	5.318	0.021
M5	7.331	-1.991	5.340	-0.567
M6	6.773	-1.281	5.492	-0.009
M8	6.734	-1.605	5.129	0.03
M9	6.74	-1.468	5.272	0.024