Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Exploring the Effect of C_6H_{5-x}/F_xBr (x=0~3) Passivating Agent on Surface Properties at Different Termination: First principles

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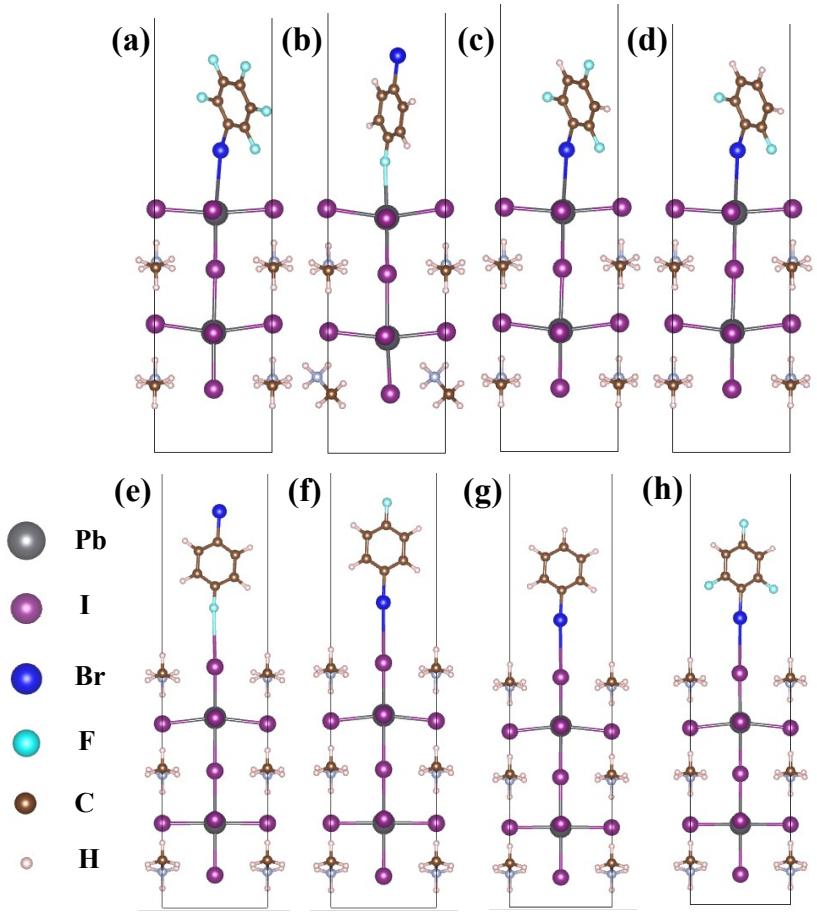

Fig. S1. Passivation models for different terminals of perovskite. (a)-(d) represents the addition of BrPFB, 4-F-BrB, 2-4-6-F-BrB and 2-6-F-BrB on the PbI2-terminated surface. (e)-(h) represents the addition of 4-F-BrF, 4-Br-BrF, BrB and 2-4-6-F-BrB on the MAI-terminated surface.

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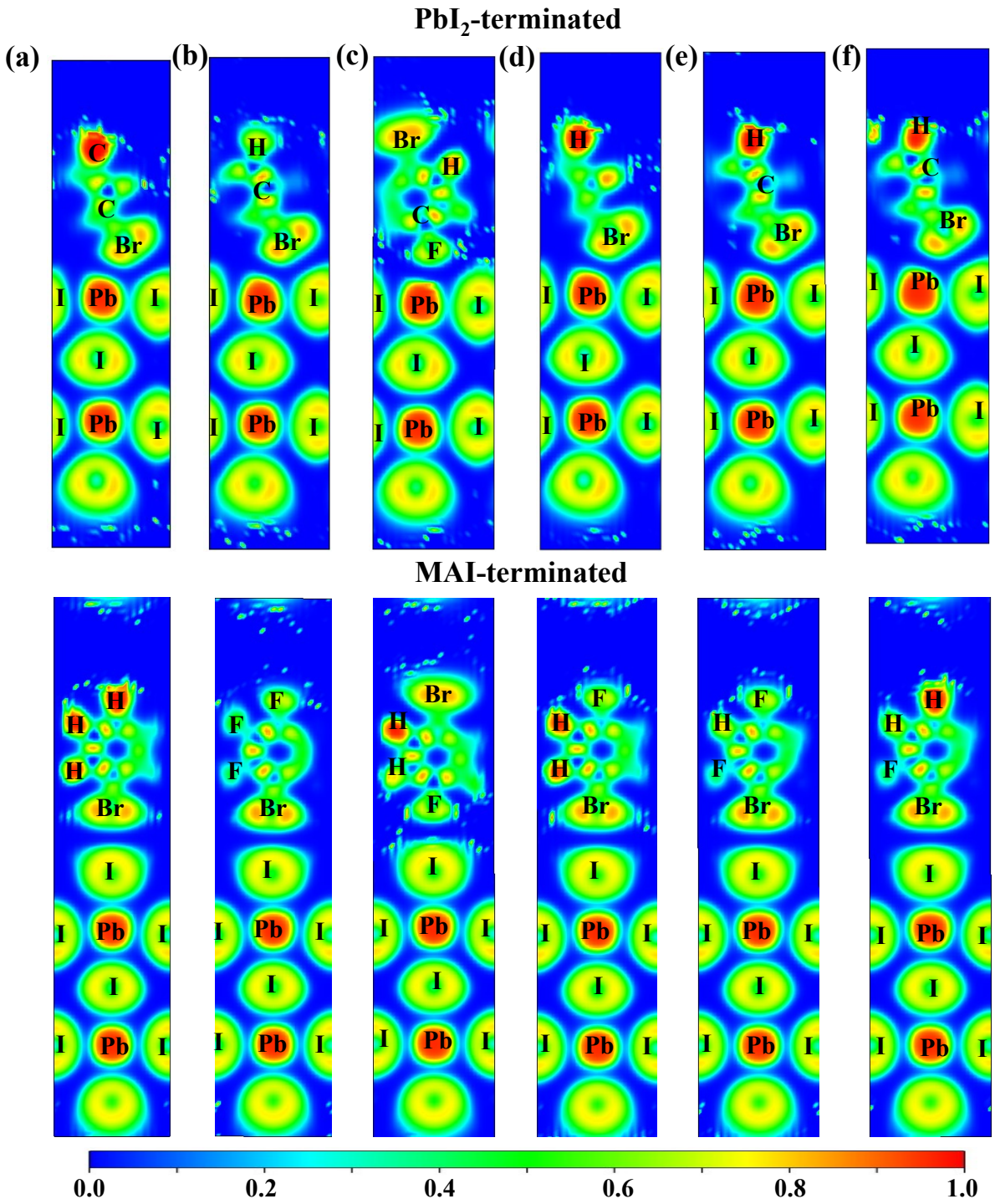

Fig. S2. The side view of the electron localization function at PbI_2 and MAI terminated surface, (a)-(f) adsorbed BrB, BrPFB, 4-F-BrB, 4-Br-FB, 2-4-6-F-BrB, and 2-6-F-BrB, respectively. The threshold range of the contour line is [0 (blue), 1 (red)], where 1 represents complete positioning and 0 represents incomplete positioning.

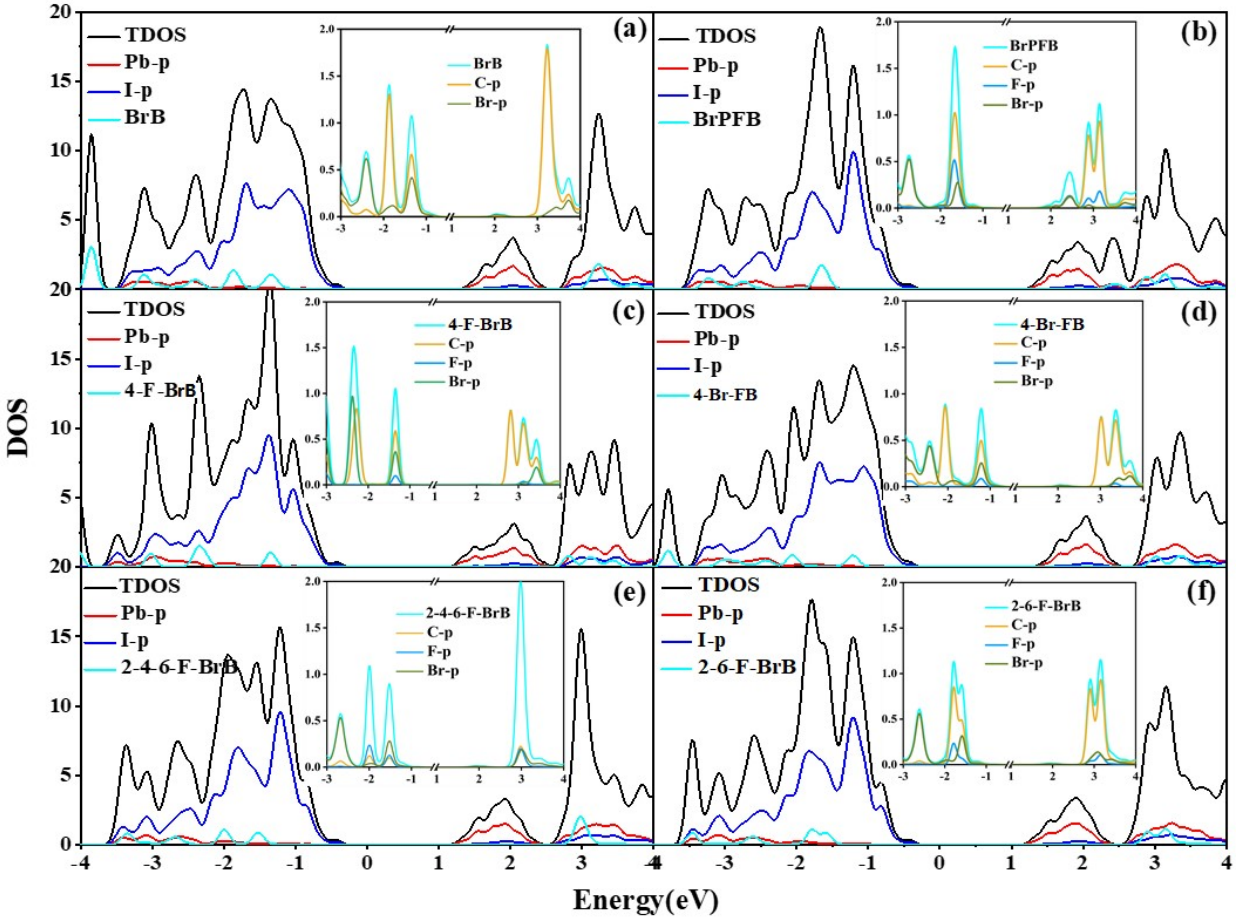

Fig. S3. The partial densities of states at the MAI-terminated surface with the addition of BrB, BrPFB, 4-F-BrB, 4-Br-FB, 2-4-6-F-BrB, and 2-6-F-BrB, respectively.

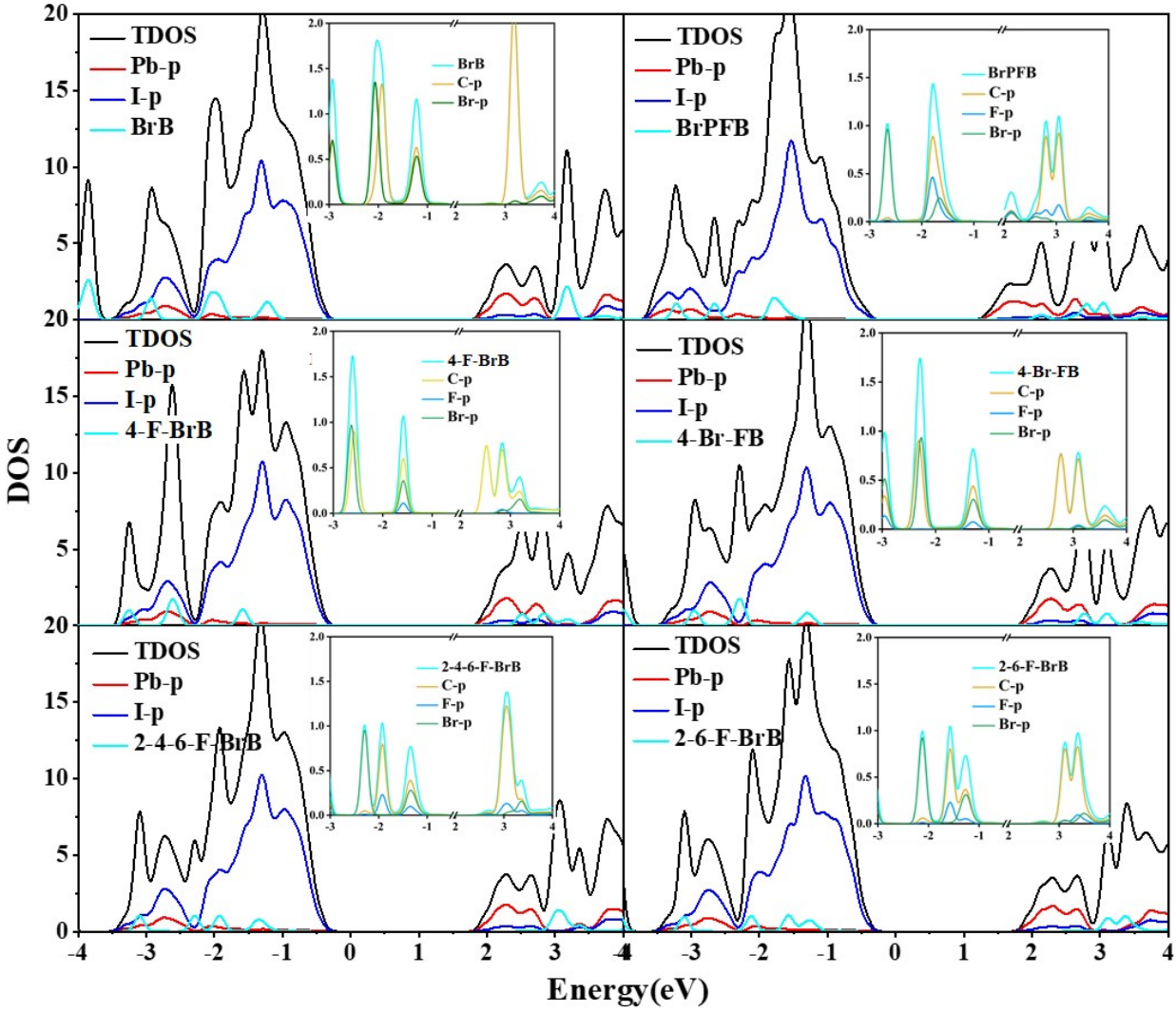

Fig. S4. The partial densities of states at the PbI_2-terminated surface with the addition of BrB, BrPFB, 4-F-BrB, 4-Br-FB, 2-4-6-F-BrB, and 2-6-F-BrB, respectively.

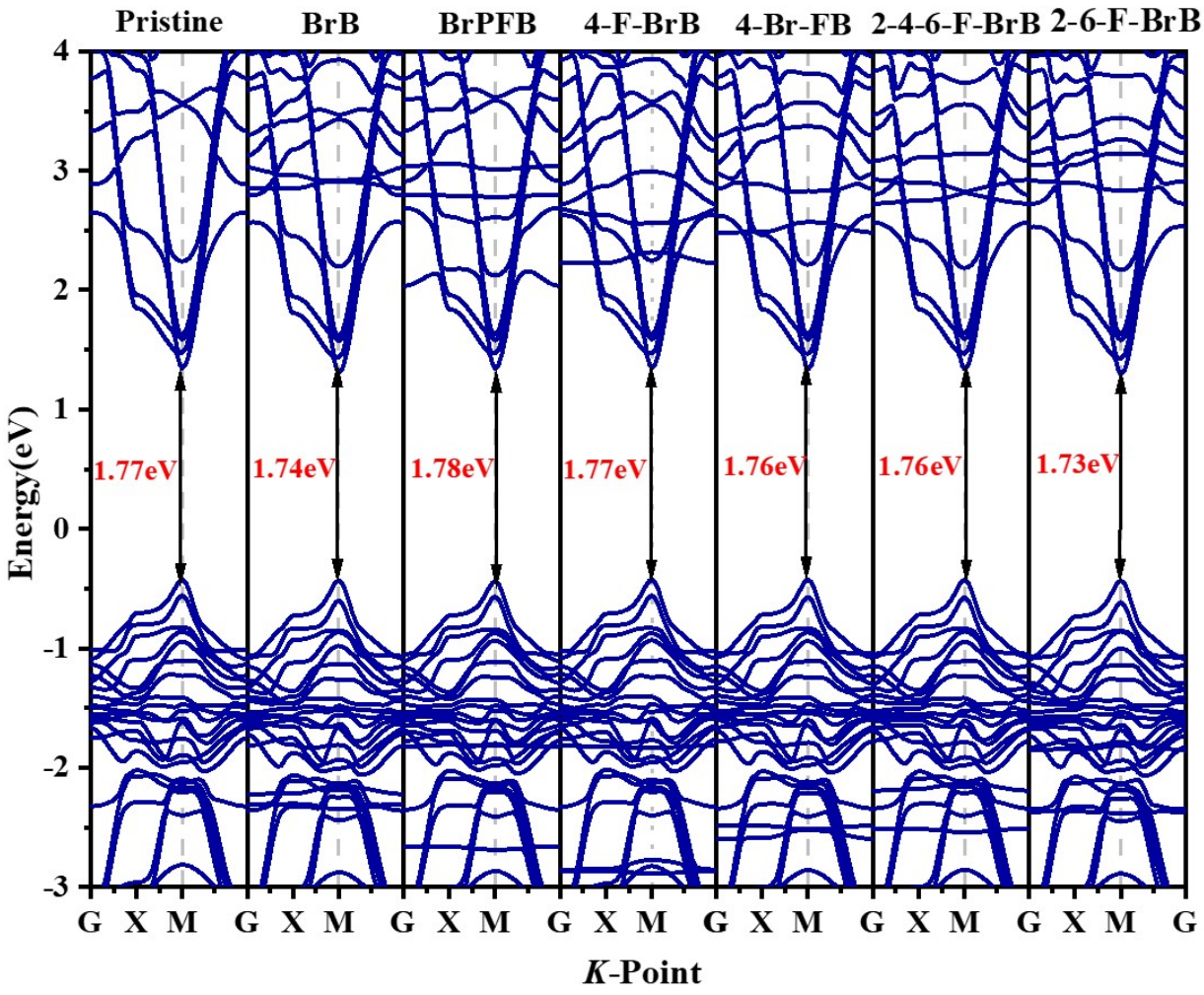

Fig. S5. Band structures is displayed at the MAI-terminated surface with the addition of BrB, BrPFB, 4-F-BrB, 4-Br-FB, 2-4-6-F-BrB, and 2-6-F-BrB, respectively.

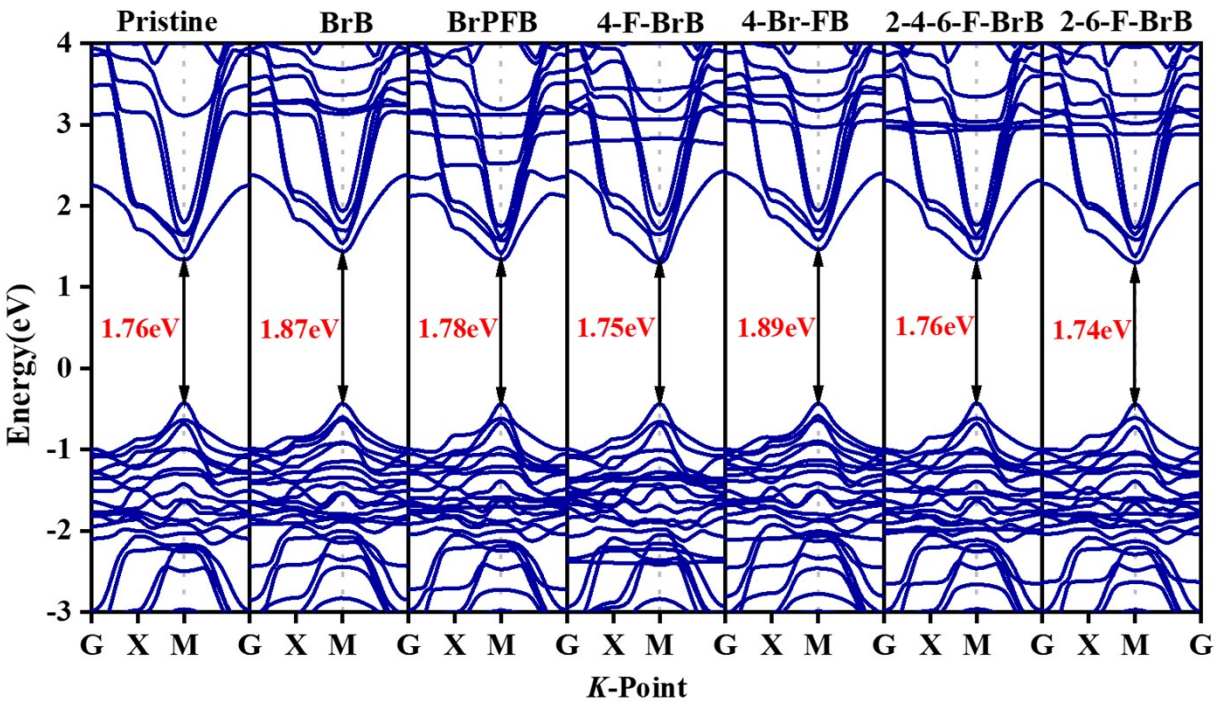

Fig. S6. Band structures is displayed at the PbI_2-terminated surface with the addition of BrB, BrPFB, 4-F-BrB, 4-Br-FB, 2-4-6-F-BrB, and 2-6-F-BrB, respectively.

Table S1. The energy values of LUMO and HOMO of different molecules and the energy values of global reaction activity.

Molecule	HOMO(eV)	LUMO(eV)	ΔE(eV)
BrB	-6.05	-1.51	4.55
BrPFB	-6.75	-2.44	4.31
4-Br-FB	-6.07	-1.85	4.22
2-4-6-F-BrB	-6.39	-1.90	4.49
2-6-F-BrB	-6.35	-1.85	4.50

Table S2. Bader changes on the MAI- and PbI_2- terminated surface, for passivated molecules, undercoordinated Pb, and I atoms.

Terminated	Charge	BrB	BrPFB	4-F-BrB	4-Br-FB	2-4-6-F-BrB	2-6-F-BrB
MAI	Molecule	0.073	0.008	0.186	0.185	0.066	0.161
	Pb	0.855	-0.858	-0.842	-0.851	-0.844	-0.847
	I	0.569	-0.567	0.566	0.567	0.564	0.566
PbI_2	Molecule	0.055	0.005	0.203	0.284	-0.030	0.160
	Pb	-0.900	-0.894	-0.892	-0.883	-0.893	-0.916
	I	0.553	0.545	0.547	0.548	0.547	0.188

Table S3 Electron (m_e) and hole (m_h) effective masses, the reduced effective mass(μ), high-frequency dielectric constants (ε) and exciton binding energies (E_g) on the different terminations after adding passivators and the intrinsic structure.

Terminate	Compounds	$m_e(m_0)$		$m_h\ (m_0)$		μ	ε	Eb（meV）
		Γ–*X*	***Γ***–*M*	***Γ***–*X*	***Γ***–*M*			
MAI	*Cell*	0.665	0.280	0.239	0.168	0.142	2.414	0.332
				m*=0.11me				
	BrB	0.724	0.274	0.245	0.165	0.145	2.674	0.276
	BrPFB	0.825	0.280	0.267	0.167	0.156	2.697	0.292
	4-F-BrB	0.748	0.279	0.240	0.168	0.146	2.663	0.2801
	4-Br-FB	0.834	0.278	0.249	0.165	0.151	2.678	0.287
	2-4-6-F-BrB	0.888	0.279	0.255	0.165	0.154	2.687	0.290
	2-6-F-BrB	0.788	0.278	0.252	0.165	0.150	2.680	0.284
PbI_2	*Cell*	0.975	0.248	0.325	0.562	0.257	4.433	0.178
	BrB	0.724	0.274	0.245	0.165	0.145	3.170	0.196
	BrPFB	0.825	0.280	0.267	0.167	0.156	3.334	0.191
	4-F-BrB	0.748	0.279	0.240	0.168	0.146	3.231	0.190
	4-Br-FB	0.834	0.278	0.250	0.165	0.151	3.163	0.205
	2-4-6-F-BrB	0.888	0.279	0.255	0.165	0.154	3.305	0.192
	2-6-F-BrB	0.788	0.278	0.252	0.165	0.150	3.302	0.187

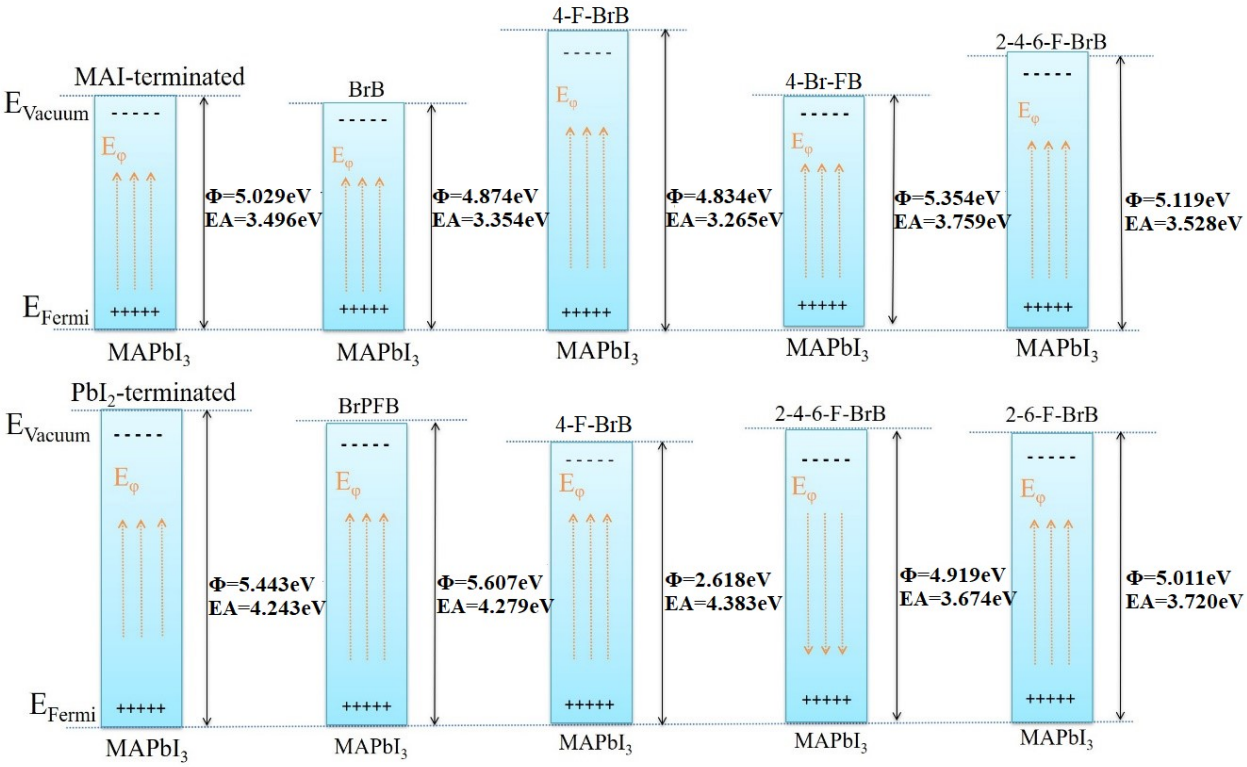

Fig. S7. The surface work function of the intrinsic structure and the electron affinity potential(EA) after adsorbing BrB, 4-F-BrB, 4-Br-FB and 2-4-6-F-BrB on the MAI-terminated surface and adsorbing BrPFB, 4-F-BrB, 2-4-6-F-BrB, and 2-6-F-BrB on the PbI2-terminated surface.

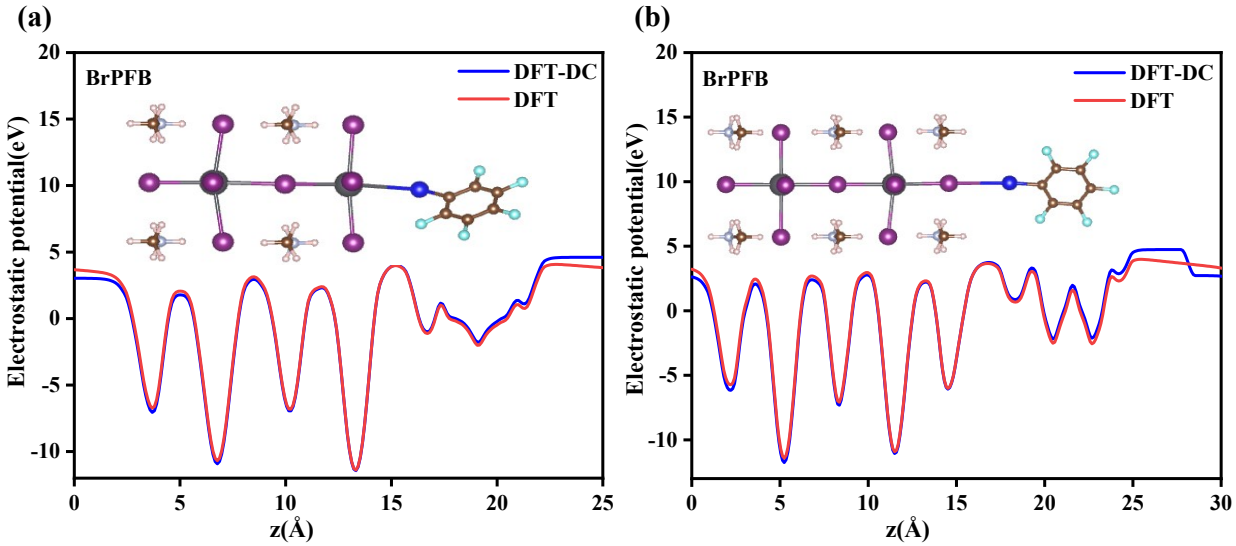

Fig. S8. (a) and (b) are the average planar potentials for adsorbing BrPFB at the PbI_2-terminated and MAI-terminated surfaces, respectively. Blue refers to adding dipole correction during calculation, while red refers to using DFT instead of adding dipole correction during calculation.

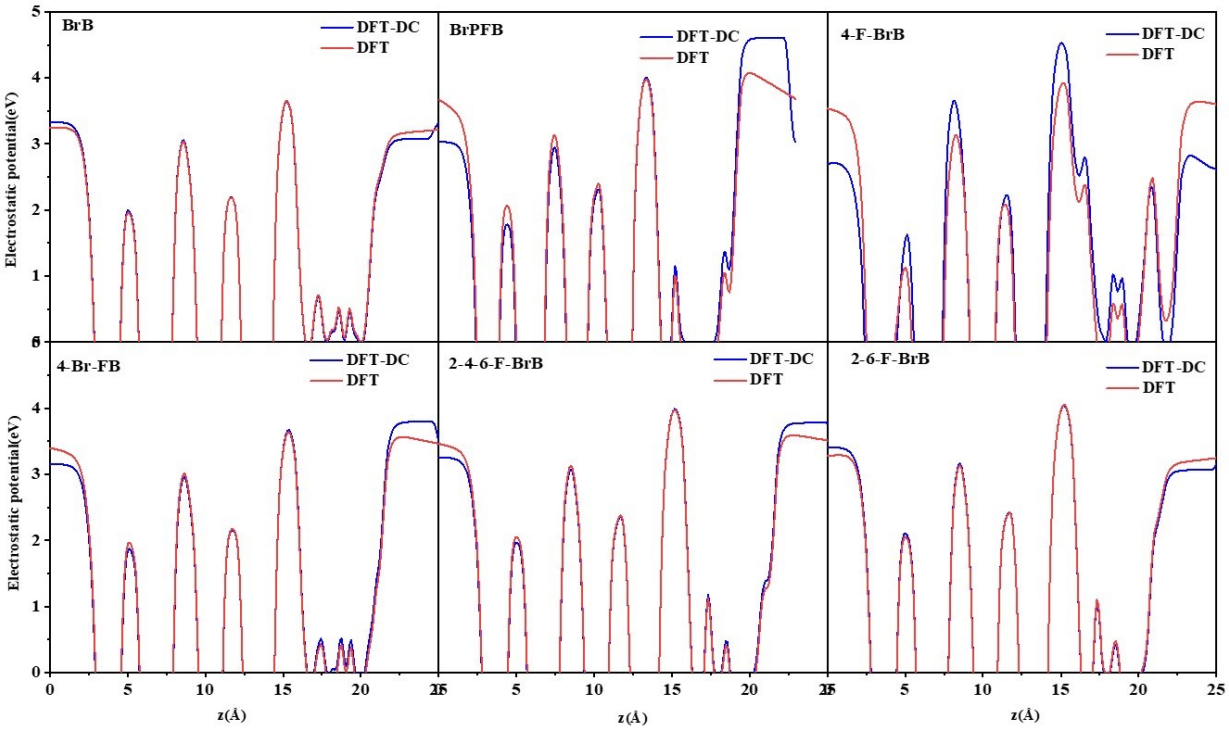

Fig. S9. The difference in the planar average potential calculated using dipole correction in the adsorption of small molecules with different F contents at the PbI_2-terminated surfaces. Blue refers to adding dipole correction during calculation, while red refers to using DFT instead of adding dipole correction during calculation.

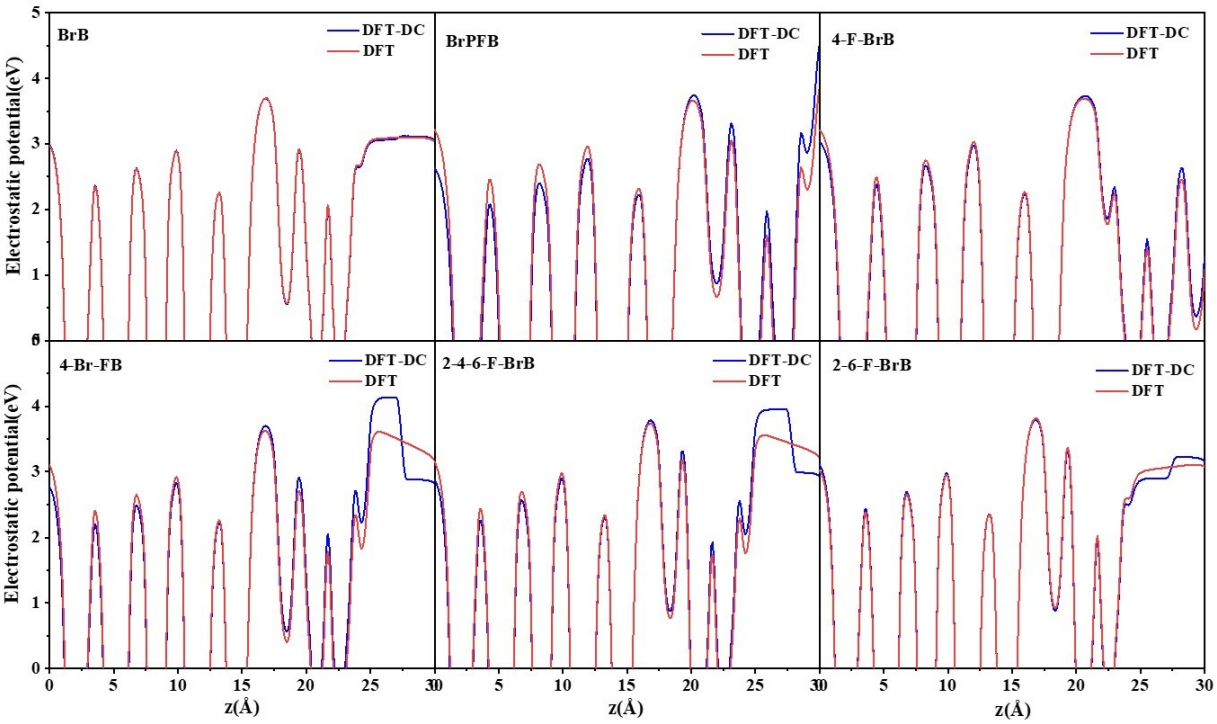

Fig. S10. The difference in the planar average potential calculated using dipole correction in the adsorption of small molecules with different F contents at the MAI-terminated surfaces. Blue refers to adding dipole correction during calculation, while red refers to using DFT instead of adding dipole correction during calculation.