Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Recipe for the Design of Mixed Cation Lead Halide Perovskite: Adsorption and Charge Transfer from A-site Cations to PbI_2

Hongfei Chen[a], Hejin Yan[a], Yongqing Cai[a]*

[a]*Joint Key Laboratory of the Ministry of Education, Institute of Applied Physics and Materials Engineering, University of Macau, Taipa, Macau, China*

*Corresponding author: yongqingcai@um.edu.mo

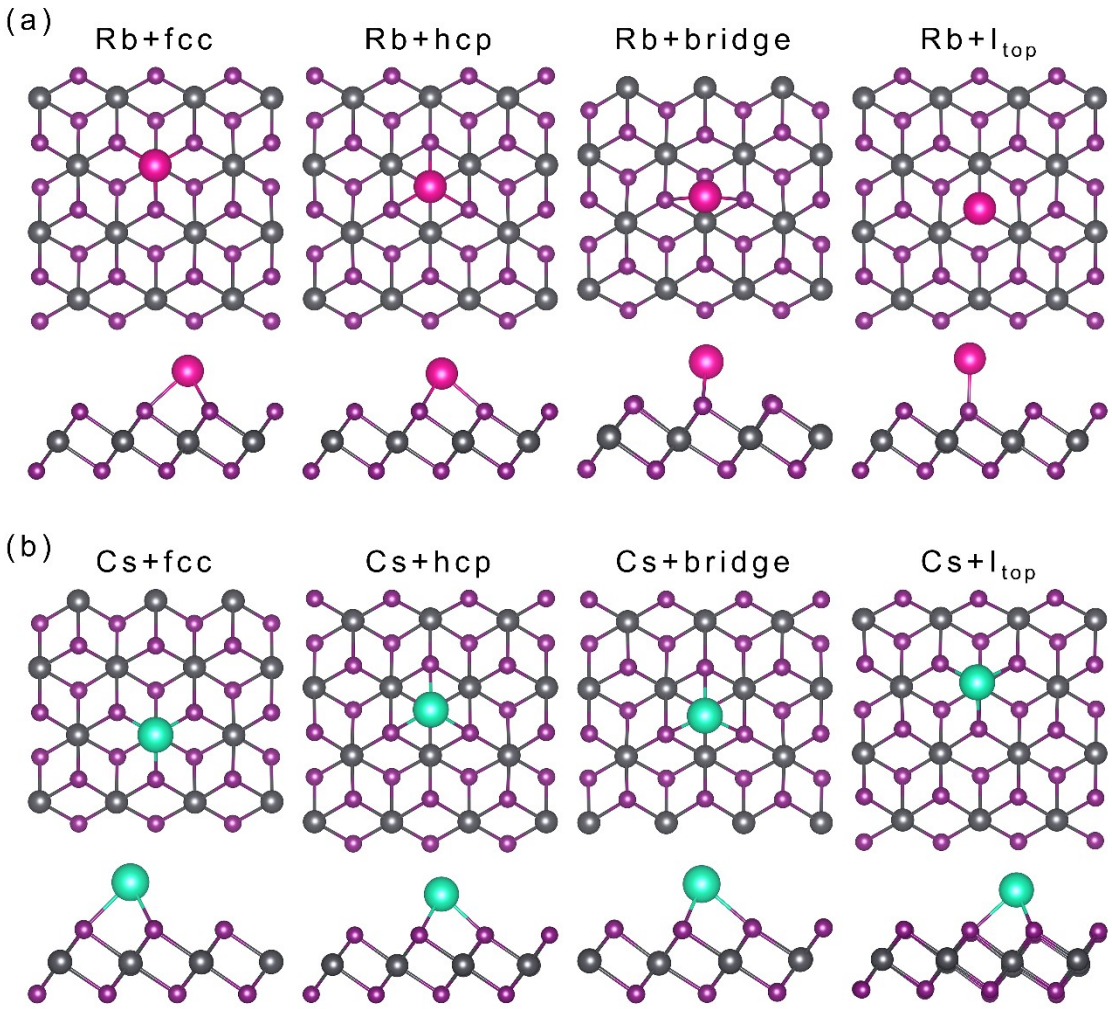

Figure S1. The relaxed configurations of inorganic a) Rb+ and b) Cs+ adsorbed on PbI_2 in different interactive sites.

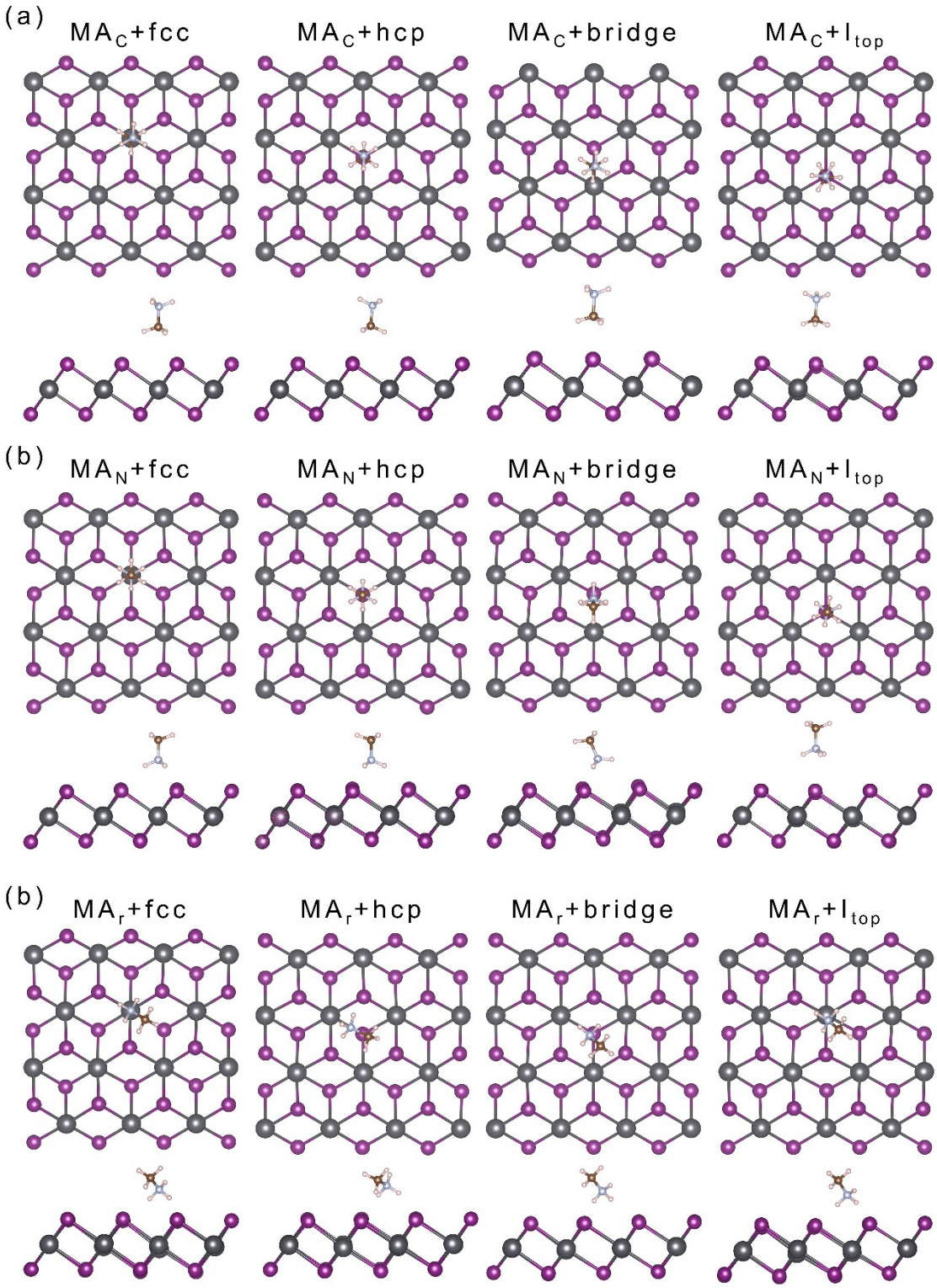

Figure S2. The relaxed configurations of organic MA cation adsorbed on PbI_2 in different interactive sites. a) The $-CH_3$ side of MA cation is designed close to PbI_2, denote as MA_c. b) The ammonia group of MA cation are designed close to PbI_2, denote as MA_N. (b) The MA cation is designed as recline related to PbI_2, denote as MA_r.

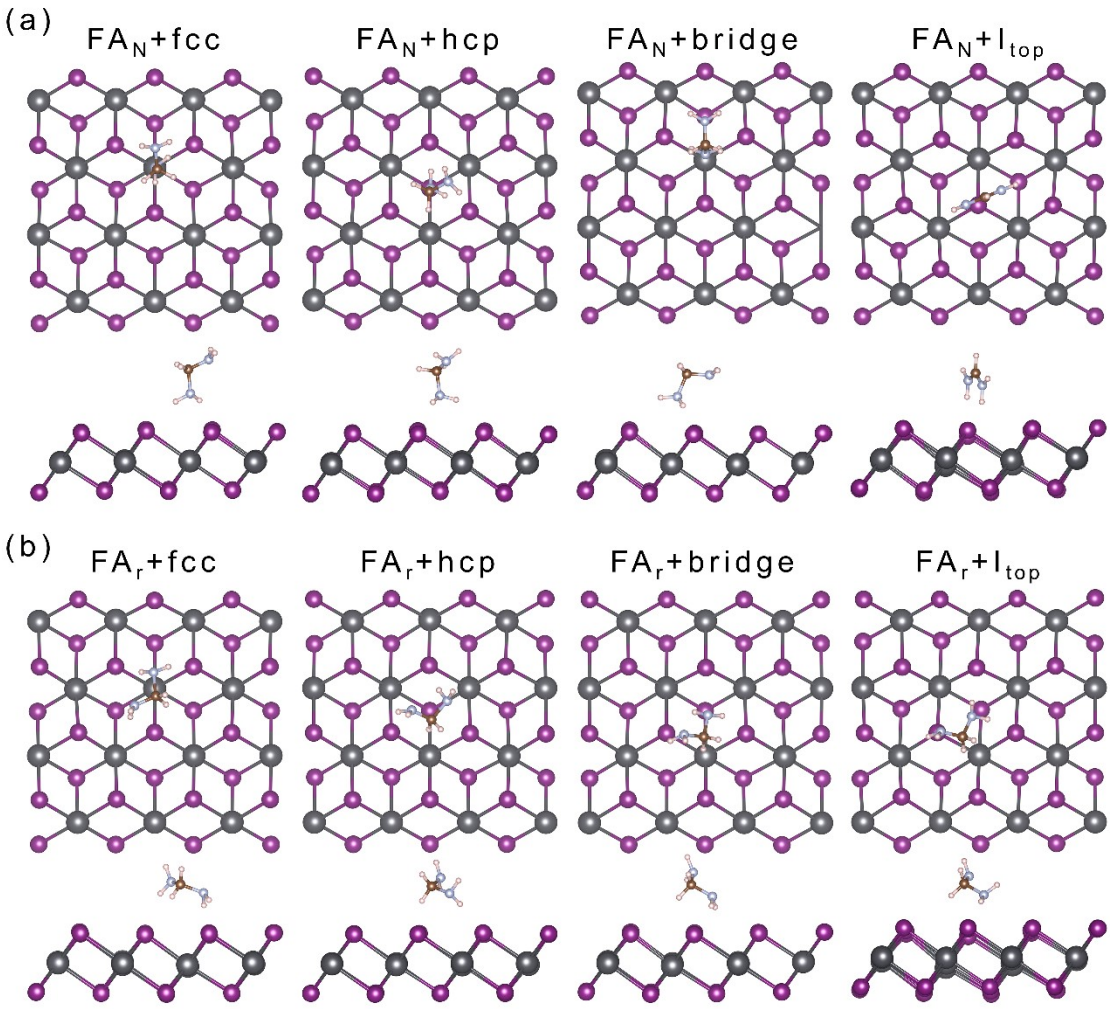

Figure S3. The relaxed configurations of organic FA cation adsorbed on PbI_2 in different interactive sites. a) The ammonia group of FA cation are designed close to PbI_2, denote as FA_N. (b) The FA cation is designed as recline related to PbI_2, denote as $FA_{r.}$

Table S1. Energy information of all considered adsorption configurations. Bold text indicates the lowest-energy configuration.

	fcc	hcp	bridge	Itop
Rb	-227.93	**-227.97**	-227.95	-227.54
Cs	-227.98	**-228.21**	-228.08	-228.04
MA_C	-264.13	-264.14	-264.09	-263.98
MA_N	-265.00	**-265.13**	-264.98	-264.36
MA_r	-264.88	-264.82	-264.92	-264.97
FA_N	-276.50	-276.51	-276.52	**-277.58**
FA_r	-277.00	-277.01	-277.05	-277.01

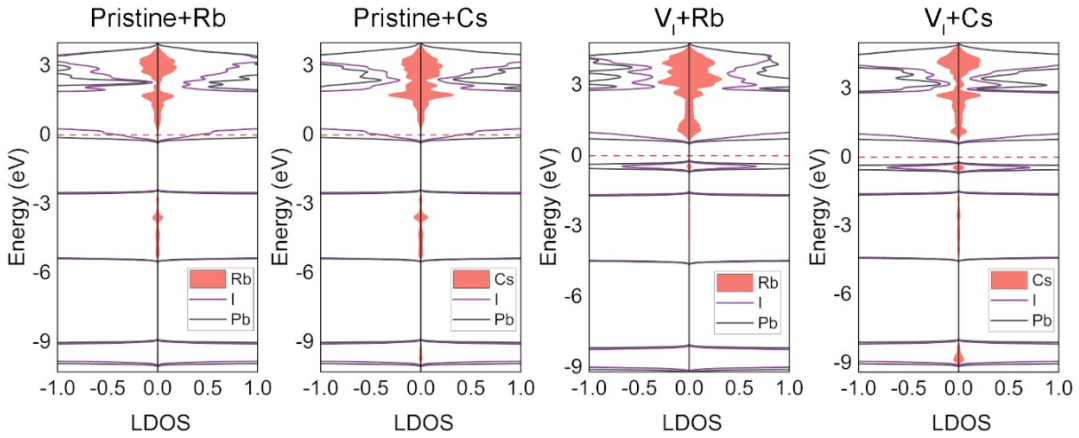

Figure S4. The whole-range LDOS for inorganic A cations (Rb and Cs) doped pristine/V_I PbI_2.

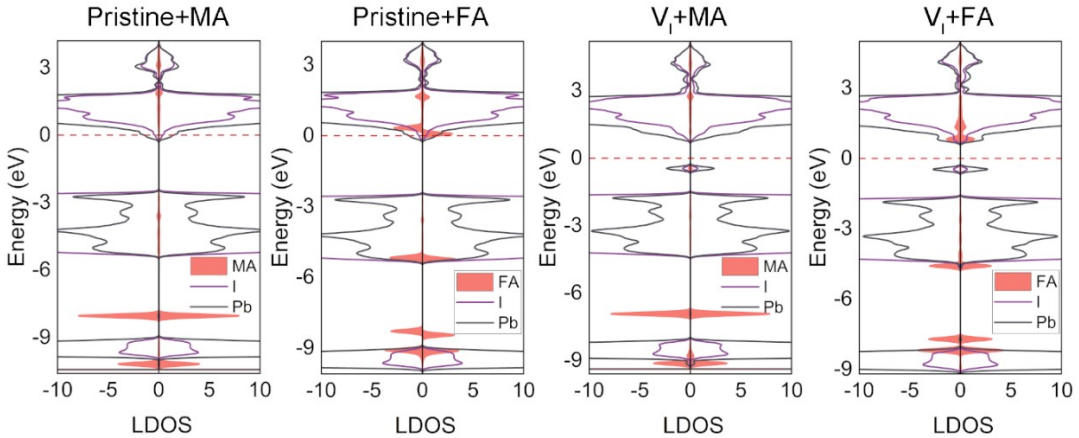

Figure S5. The whole-range LDOS for organic A cations (MA and FA) doped pristine/V_I PbI_2.

1. Bader charge

Bader charge analysis[1,2] was carried out to study the charge transfer between A cations and pristine/V_I PbI_2 substrate. Calculated values are reported in Table S2 and the trend comparison is depicted in Figure S6.

Table S2. The amount of doping electrons transferred from A cation to PbI_2 calculated using the Bader charge method and the DCD method.

A cation	Bader charge (e)		ΔQ (e)	
	Pristine	V_I	Pristine	V_I
Rb	0.87	0.93	0.44	0.54
Cs	0.87	0.86	0.46	0.31
MA	0.76	0.74	0.31	0.20
FA	0.77	0.70	0.51	0.15

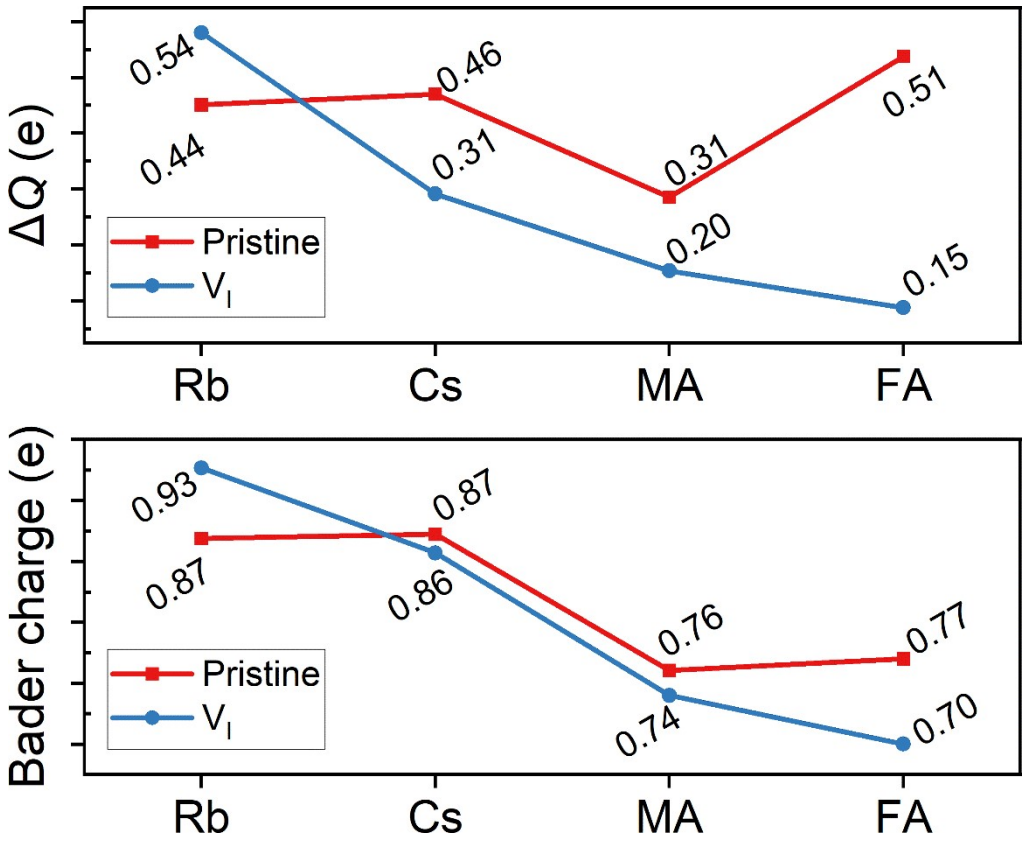

Figure S6. Comparison the total electron amount of Bader charge and DCD method for A cation doped PbI_2.

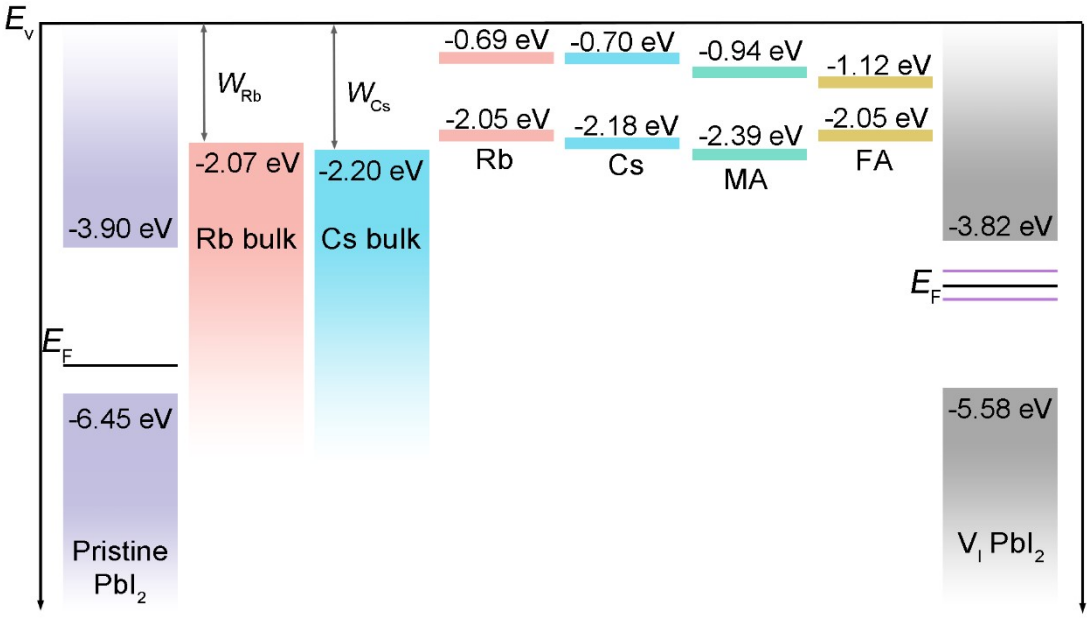

Figure S7. Energy diagram for pristine PbI_2, the work function of Rb and Cs bulk, HOMO and LOMO of Rb, Cs single atom, MA and FA molecules, $V_I PbI_2$ (from left to right). E_v is denoted as the vacuum level and E_F is the Fermi level of PbI_2. In $V_I PbI_2$ the solid purple lines represent the spin-polarized defect levels induced by V_I.

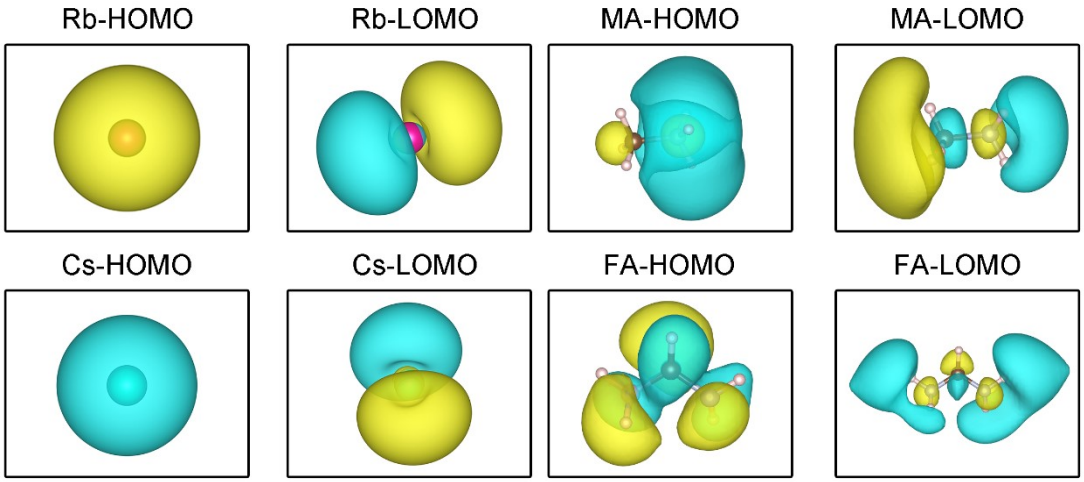

Figure S8. Charge density of HOMO and LOMO states of inorganic Rb and Cs atoms, organic MA and FA cations. Yellow and cyan plots correspond to electron–enriched and depleted regions, respectively.

REFEREFCE

(1) Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. Improved grid-based algorithm for Bader charge allocation. *J. Comput. Chem.* **2007**, *28* (5), 899–908. https://doi.org/10.1002/jcc.20575.

(2) Yu, M.; Trinkle, D. R. Accurate and Efficient Algorithm for Bader Charge Integration. *J. Chem. Phys.* **2011**, *134* (6), 064111. https://doi.org/10.1063/1.3553716.