Supplementary material

Lead-free perovskites using divalent superatom ions with tunable electronic structures and high efficiency

Tingwei Zhou（周廷伟）†, Hongling Guan（管红令）, Anlong Kuang（匡安龙）

Prof. T. Zhou, A. Kuang

Chongqing key Laboratory of Micro&Nano Structure Optoelectronics, School of Physical Science and Technology, Southwest University, Chongqing 400715, China, *Correspondence Emails: twzhou@swu.edu.cn
Prof. H. Guan
Department of Electrical and Electronic Engineering, Chongqing University of Technology, Chongqing 400054, P. R. China

Table S1. The photovoltaic parameters of single-junction solar cell for the $Cs_{0.05}(FA_{0.95}MA_{0.05})_{0.95}Pb(I_{0.95}Br_{0.05})_3$ with the direct bandgap of 1.55 eV. The correction values denoted by those with brackets.

parameters	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
References [S1]	1.1941	25.0925	89.1275	26.7069
Our work	1.262 (1.12)	27.26 (25.08)	90.2 (90.2)	31.02 (27.11)

Table S2. Calculation results of 81 cubic superatom perovskites with ABX_3 type. *Quasi cubic* represent the optimized geometry structures with lattice constants of α, β, γ (90° ± 1°) and a, b, c ($\frac{\max(a,b,c)-\min(a,b,c)}{ave(a,b,c)}\times 100\% = 0 \sim 5\%$). *Stability* indicates that the A, B, and X components remain undecomposed and exhibit negligible deformation, where × (A/B/X) represent that the collapse of A/B/X-site ion is occurred after the structure optimization. The band gaps (E_g) of these superatom perovskites are presented, with values obtained from GGA-PBE and HSE06 methods denoted by those without and with brackets, respectively.

A	B	X	perovskites	*Quasi cubic*	*Stability*	E_g (eV)
$C_3B_9H_{12}$[S2]	Al_7Li[S3]	F	$(C_3B_9H_{12})(Al_7Li)F_3$	×	√	0.94
$P(CH_3)_4$[S4]	Al_7Li[S3]	Br	$[P(CH_3)_4](Al_7Li)Br_3$	×	√	--
$C_3B_9H_{12}$[S2]	Al_7Li[S3]	I	$(C_3B_9H_{12})(Al_7Li)I_3$	×	√	0.84
$Au_3(C_3N_2H_5)_4$[S5]	$PbNa_6$[S6]	$AlBr_4$[S7]	$[Au_3(C_3N_2H_5)_4][PbNa_6](AlBr_4)_3$	×	× (B)	--
$N(CH_3)_4$[S8]	$AlSi_6$[S9]	Br	$[N(CH_3)_4](AlSi_6)Br_3$	×	× (B)	--
$N_2C_8H_{15}$[S10]	$SiLi_6$[S11]	I	$(N_2C_8H_{15})(SiLi_6)I_3$	×	× (B)	--
$N_3B_3H_3(C_3N_2H_4)_3$[S12]	$PbNa_6$[S6]	$AlBr_4$[S7]	$[N_3B_3H_3(C_3N_2H_4)_3](PbNa_6)(AlBr_4)_3$	×	× (B)	--
$P_7(C(CH_3)_3)_4$[S13]	$PbNa_6$[S6]	$AlBr_4$[S7]	$[P_7(C(CH_3)_3)_4](PbNa_4)(AlBr_4)_3$	×	× (B)	--
$N_3B_3H_3(C_3N_2H_4)_3$[S12]	$PbNa_6$[S6]	NaI_2[S14]	$[N_3B_3H_3(C_3N_2H_4)_3](PbNa_6)(NaI_2)_3$	×	× (B,X)	--
$KC_{12}O_6H_{24}$	$PbNa_6$[S6]	$AlBr_4$[S7]	$(KC_{12}O_6H_{24})(PbNa_4)(AlBr_4)_3$	×	× (B)	--
$C_6H_3(C_3N_2H_4)_3$[S12]	$PbNa_6$[S13]	$AlBr_4$[S8]	$[C_6H_3(C_3N_2H_4)_3](PbNa_4)(AlBr_4)_3$	×	× (B)	--
$C_3B_9H_{12}$[S2]	Pb_6[S15]	PF_6[S16]	$(C_3B_9H_{12})(Pb_6)(PF_6)_3$	×	√	--
Li@3^6abz[S17]	Pb_6[S15]	I	(Li@3^6abz)$(Pb_6)I_3$	×	× (B)	--
$C_3B_9H_{12}$[S2]	Pb_6[S13]	I	$(C_3B_9H_{12})(Pb_6)I_3$	×	× (B)	--
$C_3B_9H_{12}$[S2]	Pb_6 [S15]	Br	$(C_3B_9H_{12})(Pb_6)Br_3$	×	× (B)	--
$C_3B_9H_{12}$[S2]	Pb_6[S15]	BO_2[S16]	$(C_3B_9H_{12})(Pb_6)(BO_2)_3$	×	× (B)	--
$P(CH_3)_4$[S4]	**Pb_6[S15]**	**Br**	**$[P(CH_3)_4](Pb_6)Br_3$**	√	√	**0**
$N(CH_3)_4$[S8]	**Pb_6[S15]**	**Br**	**$[N(CH_3)_4](Pb_6)Br_3$**	√	√	**0**
$N(CH_3)_4$[S8]	**Pb_6[S15]**	**Cl**	**$[N(CH_3)_4](Pb_6)Cl_3$**	√	√	**0**

$P(CH_3)_4$[S4]	$Ca@C_{20}$[S18]	I	$[P(CH_3)_4](Ca@C_{20})I_3$	×	× (B)	--
$P(CH_3)_4$[S4]	$Ca@C_{20}$[S18]	F	$[P(CH_3)_4](Ca@C_{20})F_3$	×	× (B)	--
$Li@3^6abz$[S17]	$Ca@C_{20}$[S18]	I	$[Li@3^6abz](Ca@C_{20})I_3$	×	√	0.43
$Li@3^6abz$[S17]	$Ca@C_{20}$[S18]	CHO_2[S19]	$[Li@3^6abz](Ca@C_{20})(CHO_2)_3$	×	× (B)	--
$N(CH_3)_4$[S8]	Sn_6[S20]	PF_6[S21]	$[N(CH_3)_4](Sn_6)(PF_6)_3$	×	× (B)	--
$N(CH_3)_4$[S8]	Sn_6[S20]	Br	$[N(CH_3)_4](Sn_6)Br_3$	×	× (B)	--
$P(CH_3)_4$[S4]	Sn_6[S20]	BO_2[S16]	$[P(CH_3)_4](Sn_6)(BO_2)_3$	×	√	--
$N(CH_3)_4$[S8]	Si_6[S21]	F	$[N(CH_3)_4](Si_6)F_3$	×	× (B)	--
$N(CH_3)_4$[S8]	Si_6[S21]	Br	$[N(CH_3)_4](Si_6)Br_3$	×	× (B)	--
$N(CH_3)_4$[S8]	Ge_6[S20]	Br	$[N(CH_3)_4](Ge_6)Br_3$	×	× (B)	--
$C_3B_9H_{12}$[S2]	$Fe(NH_3)_6$[S22]	Br	$C_3B_9H_{12}[Fe(NH_3)_6]Br_3$	×	√	--
$NH_4@3^6abz$	$Fe(NH_3)_6$[S22]	$AlCl_4$[S7]	$NH_4@3^6abz[Fe(NH_4)_6](AlCl_4)_3$	×	√	--
$P(CH_3)_4$[S4]	$Fe(NH_3)_6$[S22]	F	$[P(CH_3)_4][Fe(NH_4)_6]F_3$	×	√	--
$C_3B_9H_{12}$[S2]	$Fe(NH_3)_6$[S22]	BF_4[S16]	$(C_3B_9H_{12})[Fe(NH_3)_6](BF_4)_3$	×	√	--
$N(CH_3)_4$[S8]	CLi_6[S11]	BF_4[S16]	$[N(CH_3)_4](CLi_6)(BF_4)_3$	×	√	--
$P_7(C(CH_3)_3)_4$[S13]	CLi_6[S11]	I	$[P_7(C(CH_3)_3)_4](CLi_6)I_3$	×	√	--
$C_5N_7H_{12}$[S23]	CLi_6[S11]	I	$(C_5N_7H_{12})(CLi_6)I_3$	×	√	--
H_3F_2@TriPip222	CLi_6[S11]	I	$(H_3F_2@TriPip222)(CLi_6)I_3$	×	× (A)	--
$KC_{12}O_6H_{24}$	CLi_6[S11]	BO_2[S16]	$(KC_{12}O_6H_{24})(CLi_6)(BO_2)_3$	×	√	--
$C_5N_7H_{12}$[S23]	CLi_6[S11]	BO_2[S16]	$(C_5N_7H_{12})(CLi_6)(BO_2)_3$	×	√	--
$N_2C_8H_{15}$[S10]	CLi_6[S11]	AlF_4[S16]	$(N_2C_8H_{15})(CLi_6)(AlF_4)_3$	×	√	--
NAl_{12}[S24]	CLi_6[S11]	F	$(NAl_{12})(CLi_6)F_3$	×	× (A)	--
PAl_{12}[S25]	CLi_6[S11]	F	$(PAl_{12})(CLi_6)F_3$	×	× (A)	--
$C_3B_9H_{12}$[S2]	**CLi_6[S11]**	**H**	**$(C_3B_9H_{12})(CLi_6)H_3$**	√	√	**0.95**
$N(CH_3)_4$[S8]	**CLi_6[S11]**	**H**	**$[N(CH_3)_4](CLi_6)H_3$**	√	√	**1.34 (1.92)**
$C_3B_9H_{12}$[S2]	**CLi_6[S11]**	**F**	**$(C_3B_9H_{12})(CLi_6)F_3$**	√	√	**0.86**
NH_4@TriPip222[S26]	**CLi_6[S11]**	**I**	**$(NH_4@TriPip222)(CLi_6)I_3$**	√	√	**1.88**
NH_4@TriPip222[S26]	CLi_6[S11]	I/Br	$(NH_4@TriPip222)(CLi_6)BrI_2$	×	√	1.83
NH_4@cryptan222[S26]	CLi_6[S11]	I	$(NH_4@cryptan222)(CLi_6)I_3$	×	√	1.97
Na@peraza222[S26]	CLi_6[S11]	I	$(Na@peraza222)(CLi_6)I_3$	×	√	1.86
K@TriPip222[S26]	**CLi_6[S11]**	**I**	**$(K@TriPip222)(CLi_6)I_3$**	√	√	**1.71**
Na@TriPip222[S17]	**CLi_6[S11]**	**I**	**$(Na@TriPip222)(CLi_6)I_3$**	√	√	**1.69**
Na@TriPip222[S17]	CLi_6[S11]	I/Br	$(Na@TriPip222)(CLi_6)BrI_2$	×	√	1.68
$NH_4@3^6abz$	**CLi_6[S11]**	**I**	**$(NH_4@3^6abz)(CLi_6)I_3$**	√	√	**1.95**
$Li@3^6abz$[S17]	**CLi_6[S11]**	**I**	**$[Li@3^6abz](CLi_6)I_3$**	√	√	**1.86**
$Li@3^6abz$[S17]	CLi_6[S11]	BO_2[S16]	$[Li@3^6abz](CLi_6)(BO_2)_3$	×	√	1.51
$NH_4@3^6abz$	CLi_6[S11]	CHO_2[S19]	$(NH_4@3^6abz)(CLi_6)(CHO_2)_3$	×	√	2.05
$C_3B_9H_{12}$[S2]	CLi_6[S11]	BH_4[S27]	$(C_3B_9H_{12})(CLi_6)(BH_4)_3$	×	√	0.54
$Li@3^6abz$[S17]	**CLi_6[S11]**	**BF_4[S16]**	**$[Li@3^6abz](CLi_6)(BF_4)_3$**	√	√	**1.97**
$Li@3^6abz$[S17]	CLi_6[S11]	BH_4[S27]	$[Li@3^6abz](CLi_6)(BH_4)_3$	×	√	2.03
$Li@3^6abz$[S17]	CLi_6[S11]	Br	$[Li@3^6abz](CLi_6)Br_3$	×	√	1.86
$AlLi_6$[S28]	**CLi_6[S11]**	**F**	**$(AlLi_6)(CLi_6)F_3$**	√	√	**(0.02)**
$AlLi_6$[S28]	**CLi_6[S11]**	**Br**	**$(AlLi_6)(CLi_6)Br_3$**	√	√	**(0.51)**
$AlLi_6$[S28]	**CLi_6[S11]**	**I**	**$(AlLi_6)(CLi_6)I_3$**	√	√	**(0.75)**

$AlLi_6$[S28]	CLi_6[S11]	BF_4[S16]	$(AlLi_6)(CLi_6)(BF_4)_3$	×	×(A)	--
$N(CH_3)_4$[S8]	CLi_6[S11]	OH	$[N(CH_3)_4](CLi_6)(OH)_3$	×	√	0.62
$N(CH_3)_4$[S8]	**CLi_6[S11]**	**C_5H_5[S29]**	**$[N(CH_3)_4](CLi_6)(C_5H_5)_3$**	√	√	**0.32 (1.00)**
$C_3B_9H_{12}$[S2]	CLi_6[S11]	C_5H_5[S29]	$(C_3B_9H_{12})(CLi_6)(C_5H_5)_3$	×	√	0.88
$P(CH_3)_4$[S4]	**CLi_6[S11]**	**C_5H_5[S29]**	**$[P(CH_3)_4](CLi_6)(C_5H_5)_3$**	√	√	**0.59 (1.17)**
$NH(CH_3)_3$[S30]	CLi_6[S11]	C_5H_5[S29]	$[NH(CH_3)_3](CLi_6)(C_5H_5)_3$	×	√	0.27 (1.00)
C_5NH_{12}[S31]	CLi_6[S11]	C_5H_5[S29]	$(C_5NH_{12})(CLi_6)(C_5H_5)_3$	×	√	0.51
NH_4	CLi_6[S11]	C_5H_5[S29]	$(NH_4)(CLi_6)(C_5H_5)_3$	×	√	0
C_4NH_{10}[S31]	CLi_6[S11]	C_5H_5[S29]	$(C_4NH_{10})(CLi_6)(C_5H_5)_3$	×	√	0.54
$C_3N_3H_8$[S32]	CLi_6[S11]	C_5H_5[S29]	$(C_3N_3H_8)(CLi_6)(C_5H_5)_3$	×	√	0
$C(NH_2)_3$	CLi_6[S11]	C_5H_5[S29]	$[C(NH_2)_3](CLi_6)(C_5H_5)_3$	×	√	0
$AlLi_6$[S28]	CLi_6[S11]	C_5H_5[S29]	$(AlLi_6)(CLi_6)(C_5H_5)_3$	×	×(A)	--
$N_2C_8H_{15}$[S10]	CLi_6[S11]	C_5H_5[S29]	$(N_2C_8H_{15})(CLi_6)(C_5H_5)_3$	×	√	0.58
$N(CH_2CH_3)_4$[S33]	CLi_6[S11]	F	$[N(CH_2CH_3)_4](CLi_6)F_3$	×	√	1.37
$N(CH_2CH_2CH_3)_4$[S33]	CLi_6[S11]	Br	$[N(CH_2CH_2CH_3)_4](CLi_6)Br_3$	×	√	1.60
$N(CH_2CH_2CH_3)_4$[S33]	CLi_6[S11]	I	$[N(CH_2CH_2CH_3)_4](CLi_6)I_3$	×	√	1.63 (2.25)
$N(CH_3)_4$[S8]	**CLi_6[S11]**	**F**	**$[N(CH_3)_4](CLi_6)F_3$**	√	√	**0.82 (1.21)**
SCs_3	**CLi_6[S11]**	**F**	**$(SCs_3)(CLi_6)F_3$**	√	√	**(1.29)**
$ClCs_3$	**CLi_6[S11]**	**F**	**$(ClCs_3)(CLi_6)F_3$**	√	√	**0**

Table S3. The lattice constants of the superatom perovskites with an unit cell and the ground state structure.

Superatom perovskites	α	β	γ	a	b	c
$(ClCs_3)(CLi_6)F_3$	90°	90°	90°	7.48	7.48	7.48

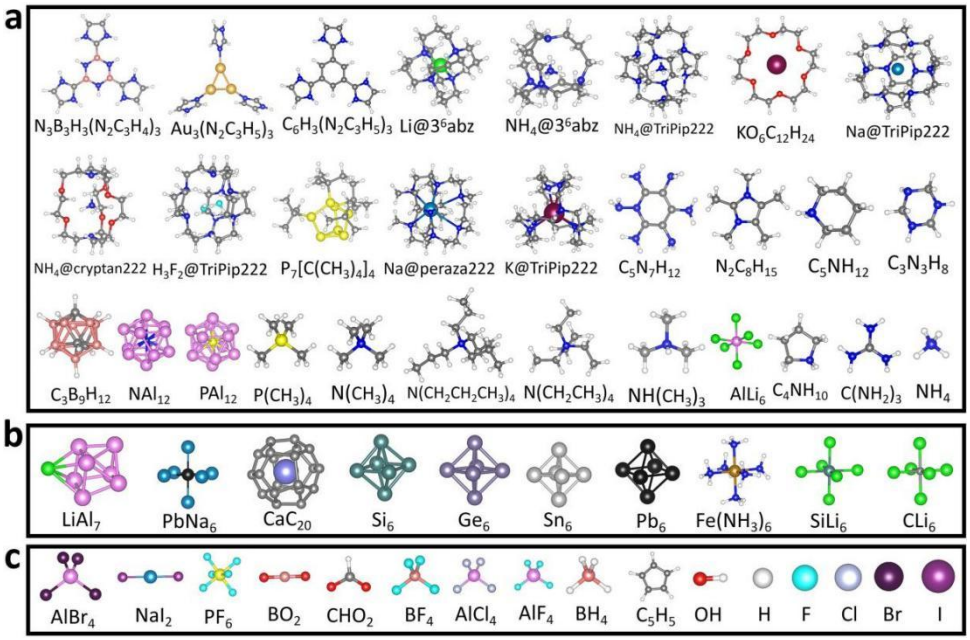

Fig. S1. (Color online) (a-c) The A, B, and X site ion structures of superatom perovskites with ABX_3 type, respectively.

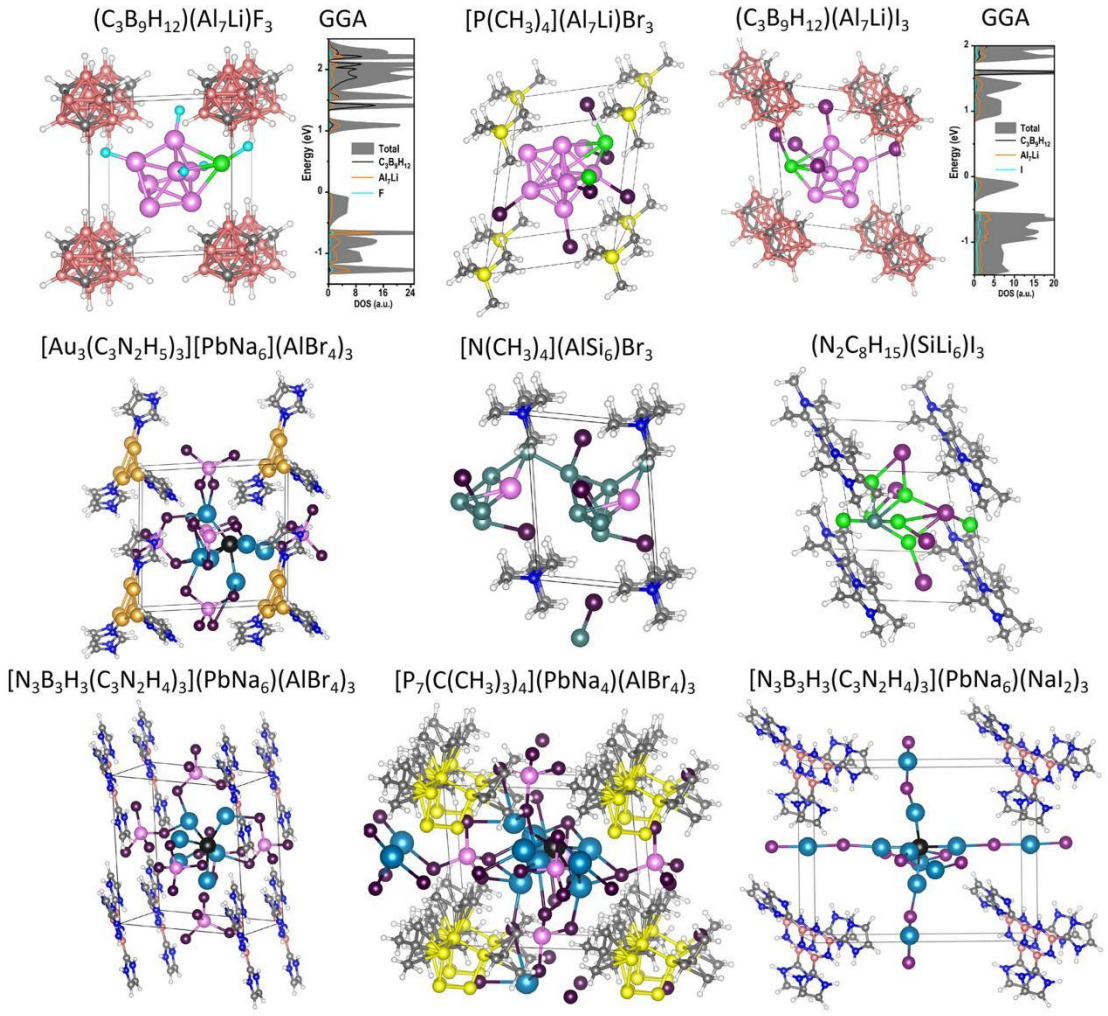

Fig. S2. (Color online) The optimized structures and density of states (DOSs) of superatom perovskites are obtained using the VASP code with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, which is based on the generalized gradient approximation (GGA). During the structural optimization of the initial cubic superatom perovskites, their lattice constants were allowed to freely relax. Additionally, for these superatom perovskites that their A, B, and X site ion structures underwent negligible structural changes following the structural optimization, their DOS calculations were performed.

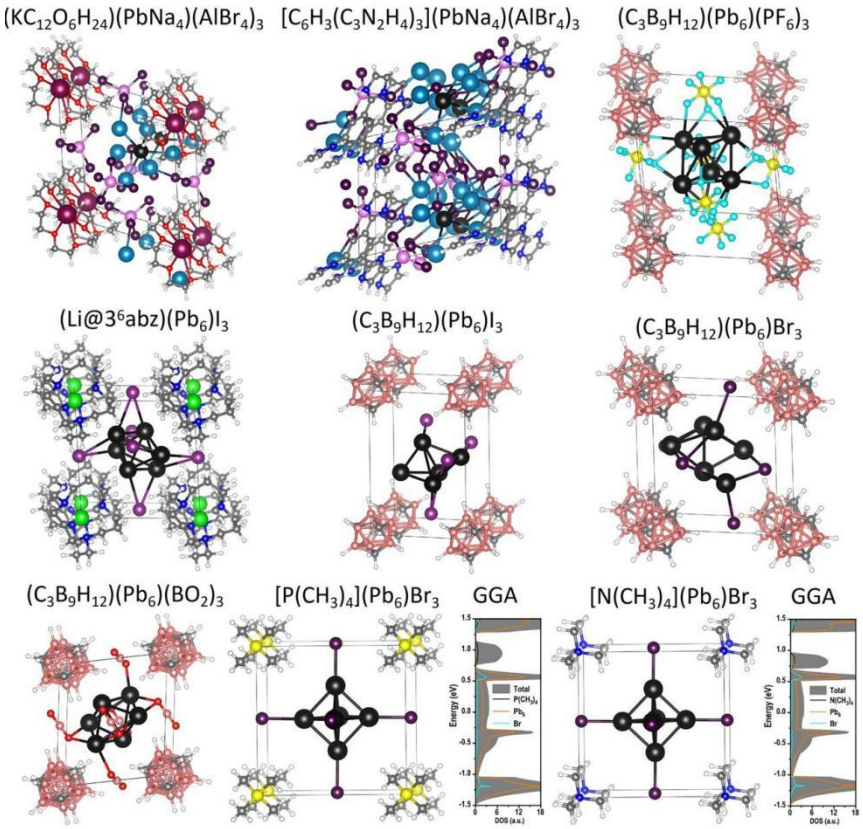

Fig. S3. (Color online) The description parallels that of Fig. S2.

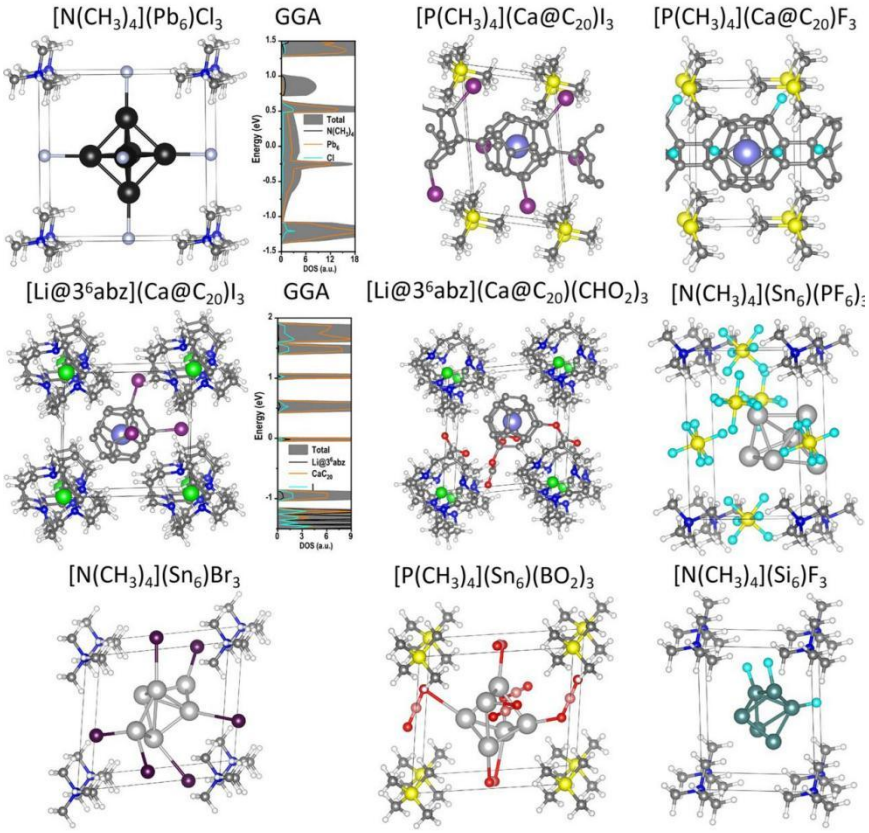

Fig. S4. (Color online) The description parallels that of Fig. S2.

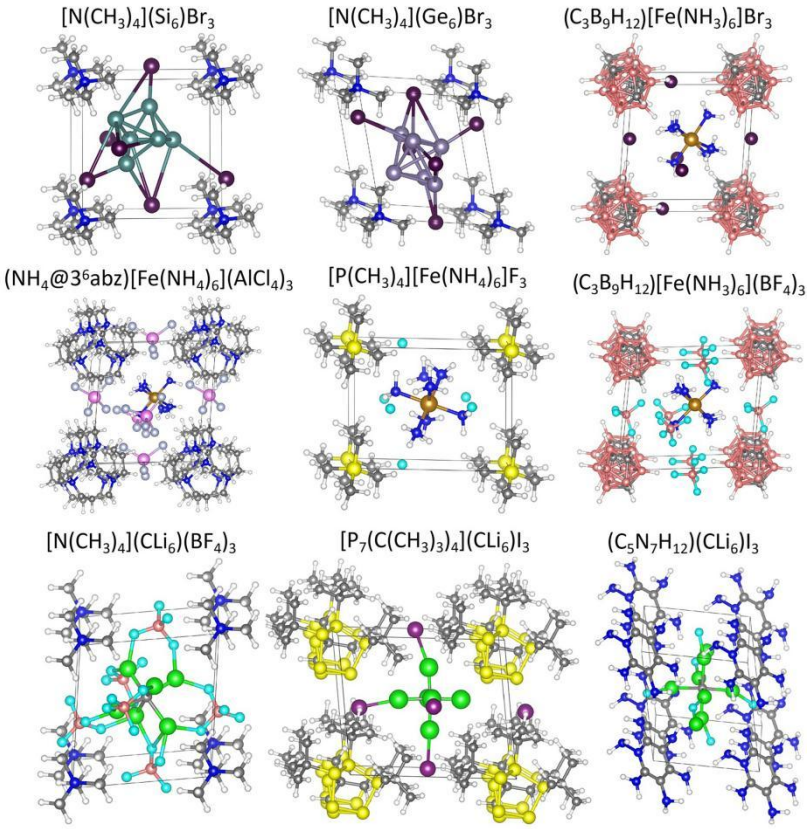

Fig. S5. (Color online) The description parallels that of Fig. S2.

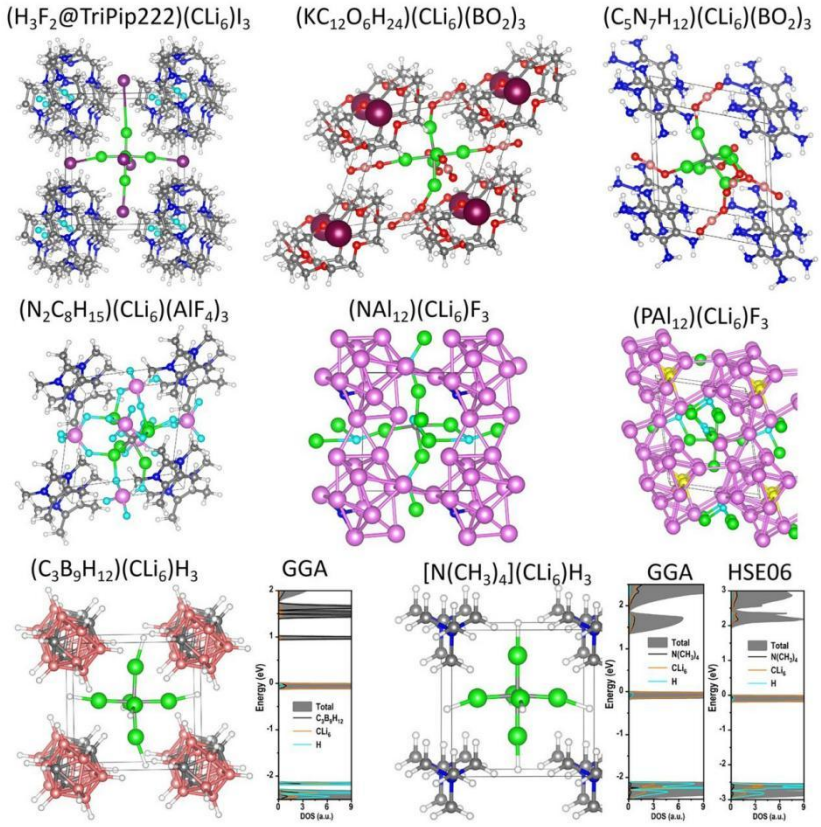

Fig. S6. (Color online) The description parallels that of Fig. S2. Herein, DOSs for $[N(CH_3)_4](CLi_6)H_3$ were calculated using the HSE06 method.

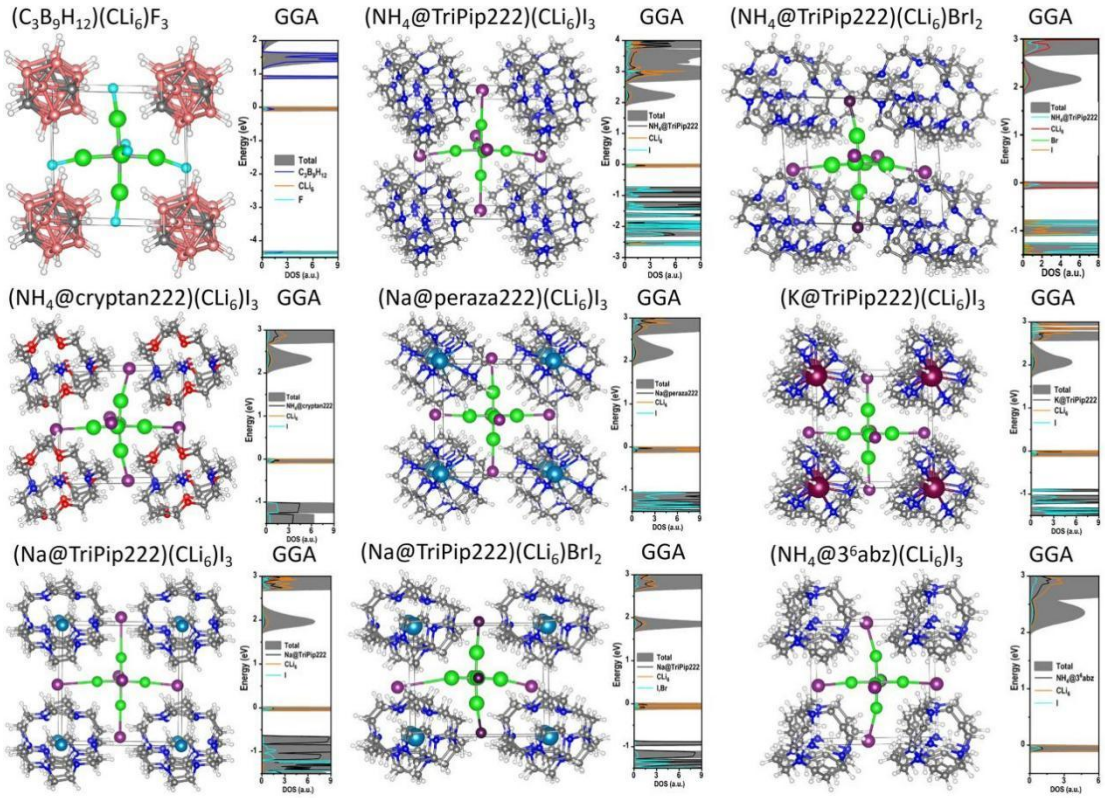

Fig. S7. (Color online) The description parallels that of Fig. S2.

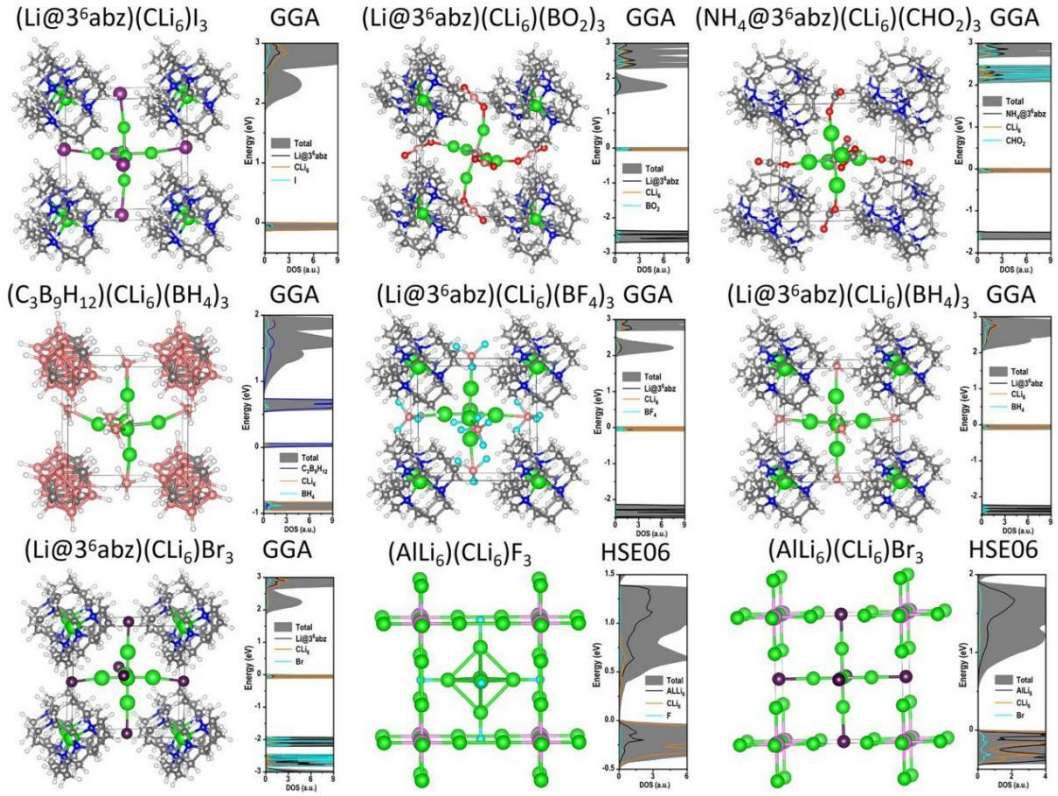

Fig. S8. (Color online) The description parallels that of Fig. S2. Herein, DOSs for $(AlLi_6)(CLi_6)F_3$ and $(AlLi_6)(CLi_6)Br_3$ were calculated using the HSE06 method.

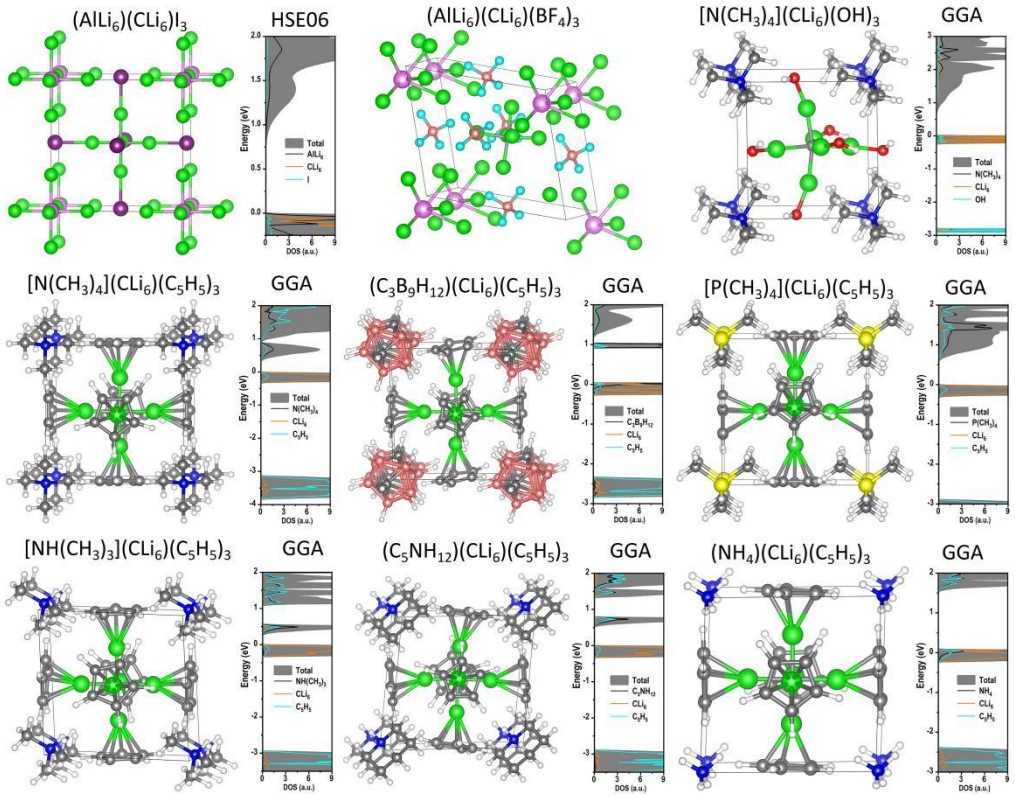

Fig. S9. (Color online) The description parallels that of Fig. S2. Herein, DOSs were calculated using the HSE06 or GGA method.

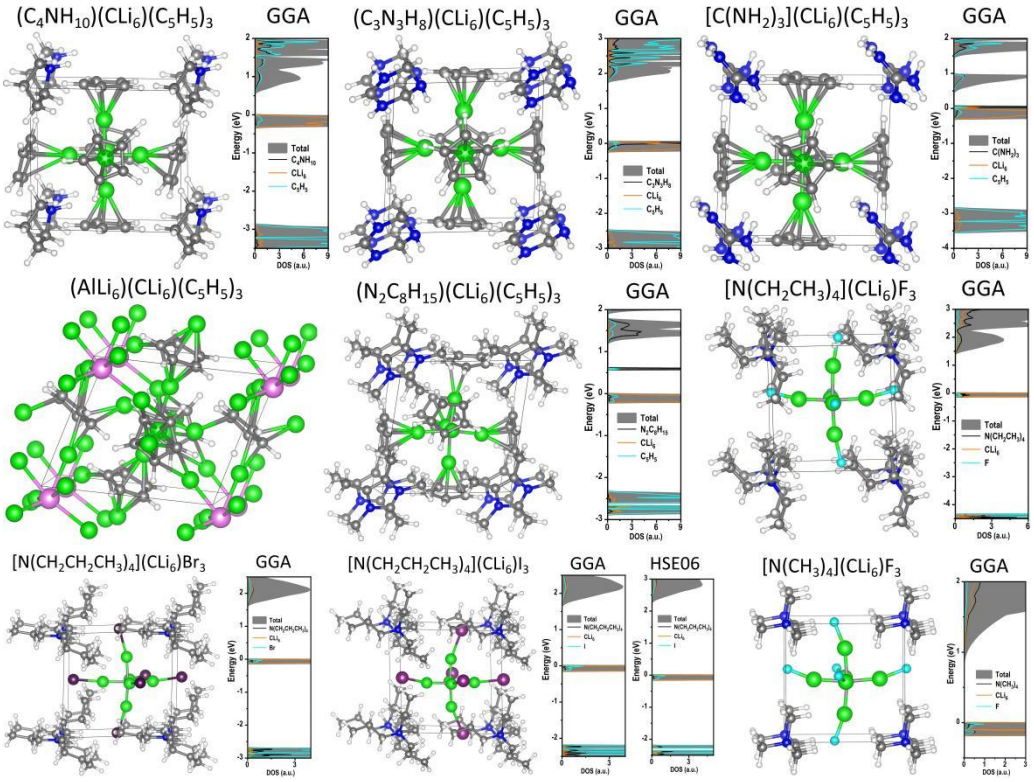

Fig. S10. (Color online) The description parallels that of Fig. S2. Herein, DOSs for $[N(CH_2CH_2CH_3)_4](CLi_6)I_3$ were calculated using the HSE06 method. Additionally, the band structure of $[N(CH_3)_4](CLi_6)F_3$ was obtained.

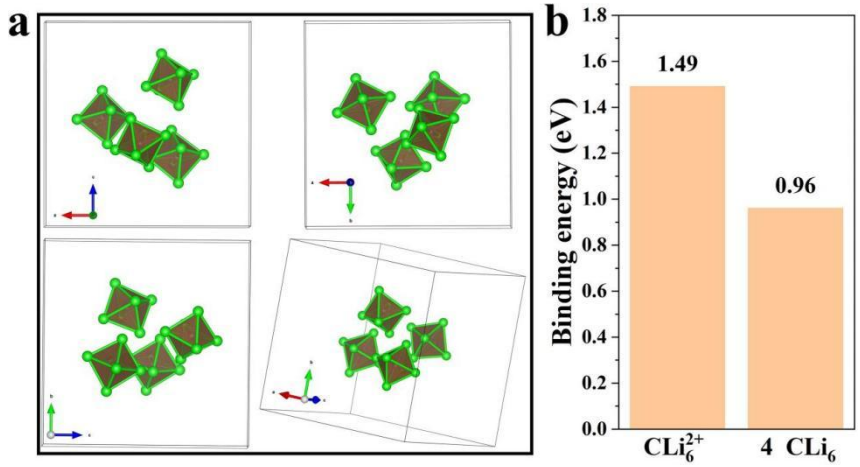

Fig. S11. (Color online) (a) Optimized structure of four CLi_6 clusters within a 15 Å cubic unit cell, employing the GGA-PBE method. (b) The average binding energy (E_{b-ave}) of the CLi_6 cluster was calculated by the equation, $E_{b-ave} = (E_{4CLi_6} - \sum_{i=1}^{4} E_{i-CLi_6})/4$, where E_{4CLi_6} and E_{i-CLi_6} are the energies of the optimized four CLi_6 clusters and single CLi_6 cluster after removing the other three clusters from four CLi_6 clusters.

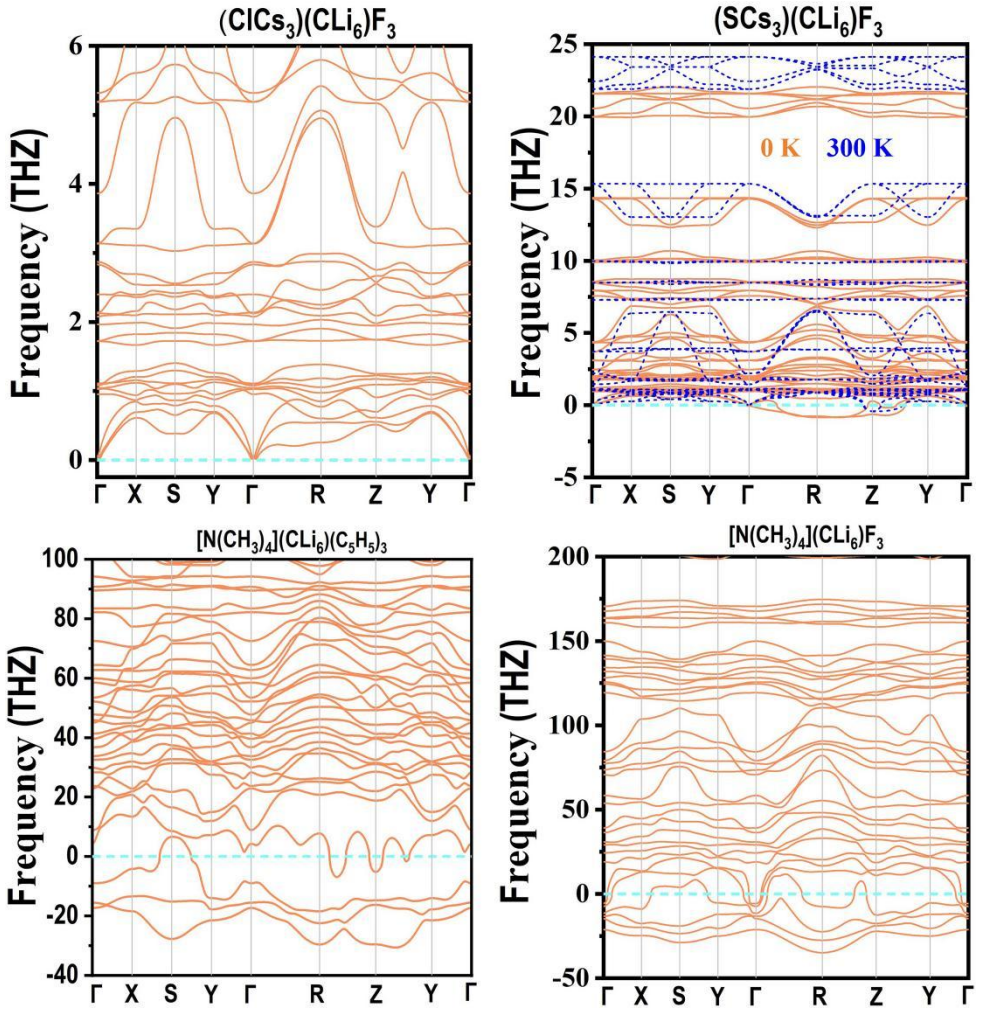

Fig. S12. (Color online) The phonon energy band structures of $(ClCs_3)(CLi_6)F_3$, $(SCs_3)(CLi_6)F_3$, $[N(CH_3)_4](CLi_6)F_3$ and $[N(CH_3)_4](CLi_6)(C_5H_5)_3$ superatom perovskites.

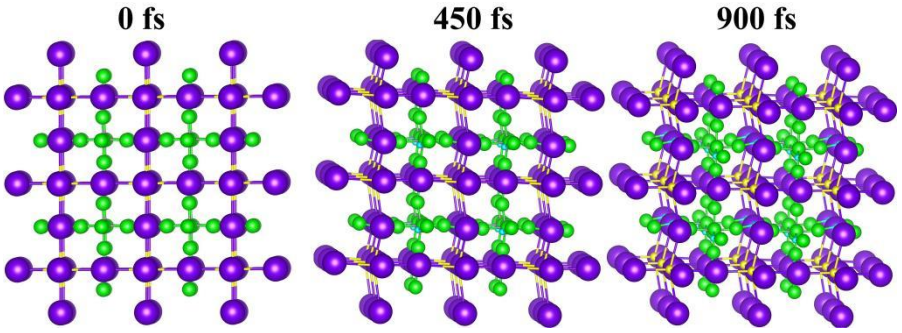

Fig. S13. (Color online) Snapshots of the $(SC_3)(CLi_6)F_3$ configuration at various time steps during the ab initio molecular dynamics simulation. The simulation was conducted over 900 fs, employing an NVT ensemble to maintain a target temperature of 300 K and a target pressure of 1 atm (10^5 Pa).

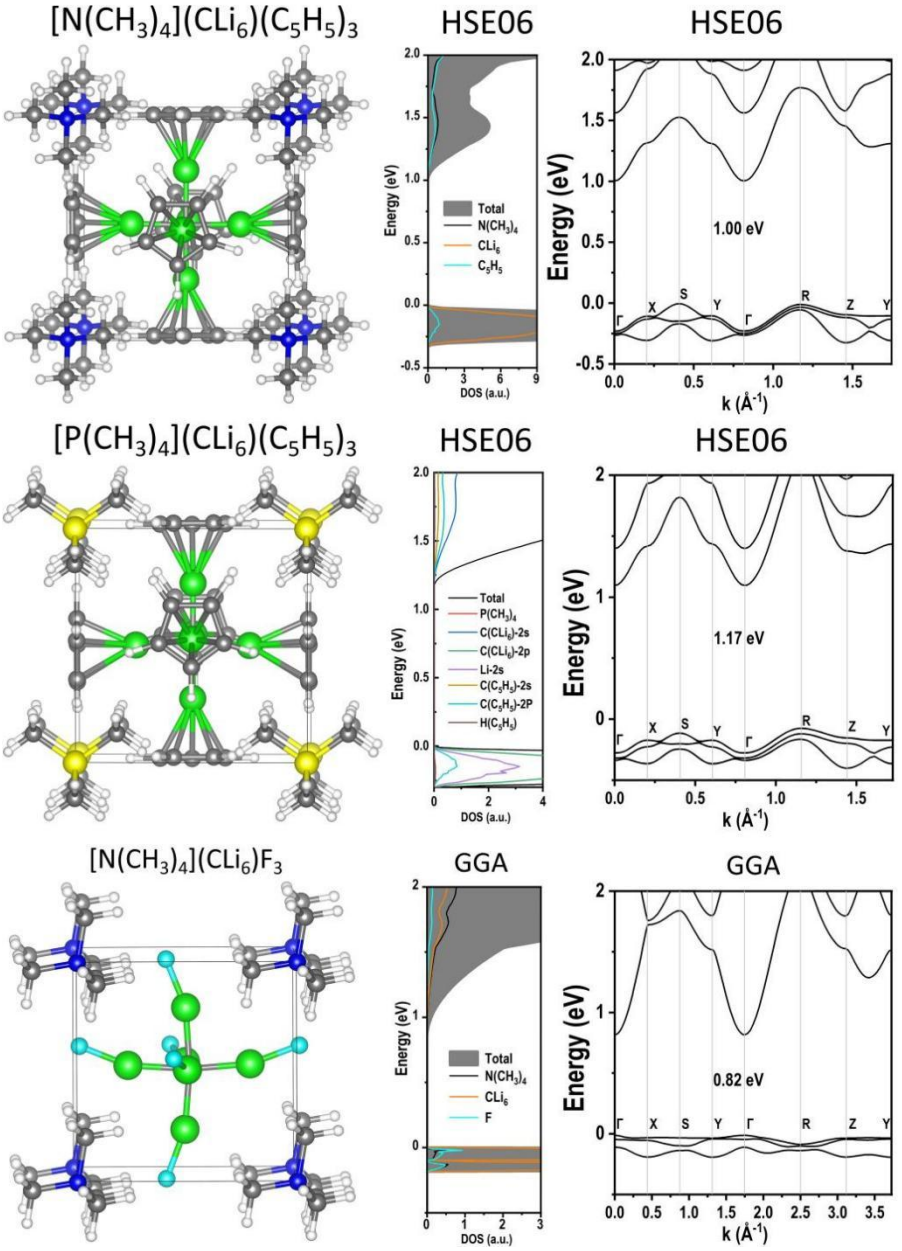

Fig. S14. (Color online) DOSs and the band structures for $[P(CH_3)_4](CLi_6)(C_5H_5)_3$ and $[N(CH_3)_4](CLi_6)F_3$ were obtained using the HSE06 method, respectively.

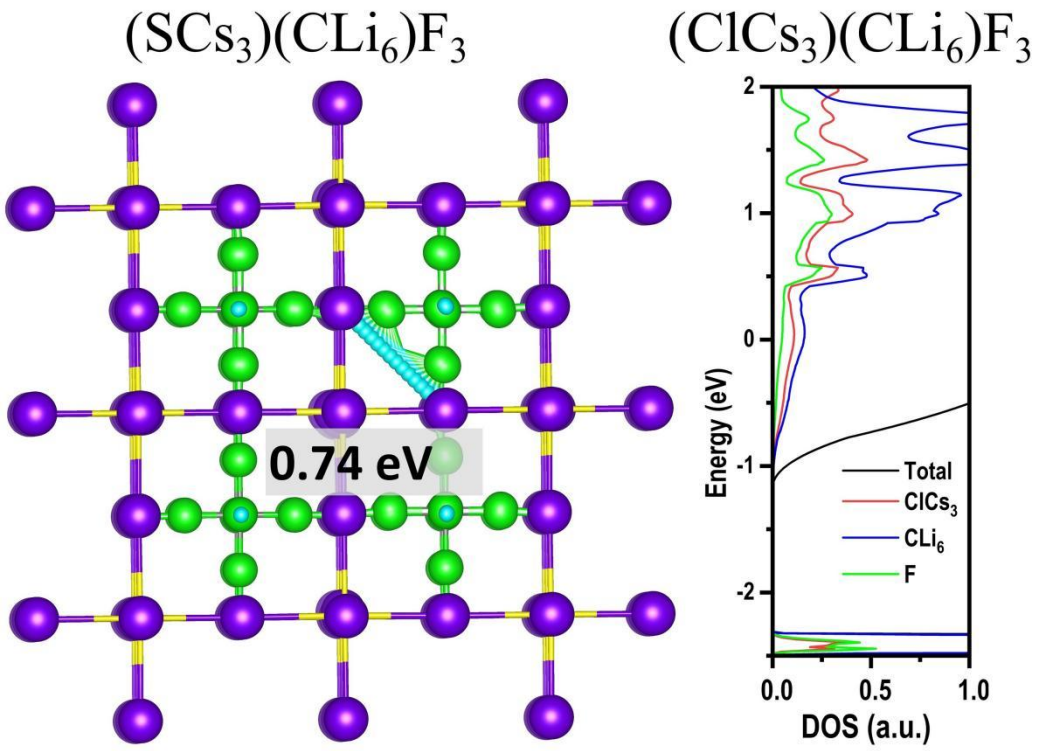

Fig. S15. (Color online) The migration energy barrier and pathway of F atom in $(SCs_3)(CLi_6)F_3$, and DOSs of $(ClCs_3)(CLi_6)F_3$ were calculated using the HSE06 method.

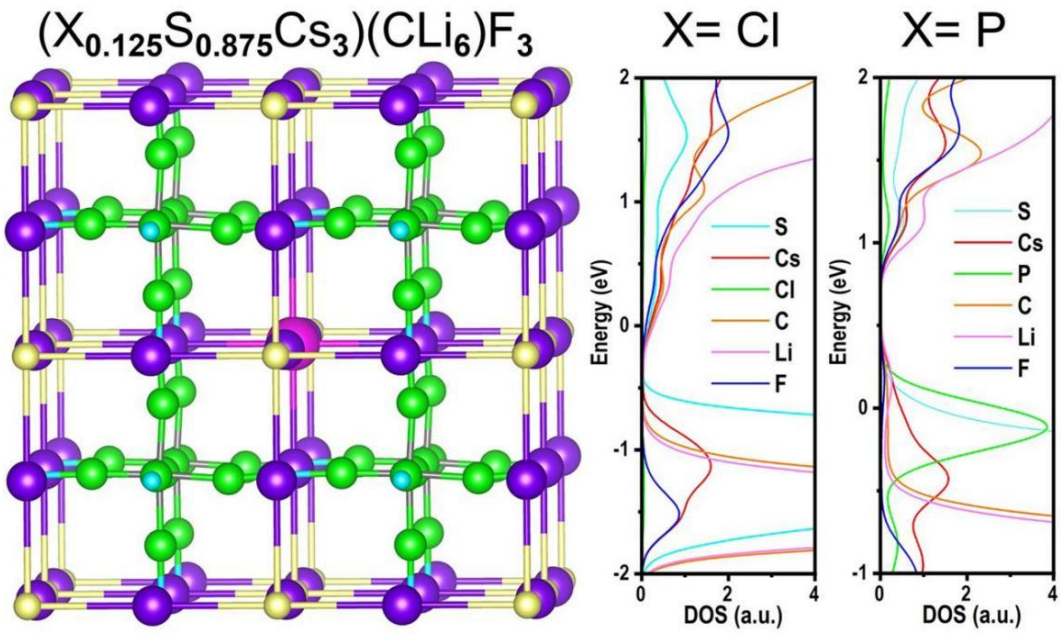

Fig. S16. (Color online) DOSs of $(X_{0.125}S_{0.875}Cs_3)(CLi_6)F_3$ were calculated using the GGA method.

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