Supporting Information

Coordinated assembly of alkali and alkaline earth metals with perfluorinated [AlF_6] group to design deep-ultraviolet zero-order waveplate materials

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Table S1. Crystal data and structure refinement for AlF_3, $BaAlF_5$, and $Li_2KAl_2F_9$.

Empirical formula	AlF_3	$BaAlF_5$	$Li_2KAl_2F_9$
Formula weight	83.98	259.32	277.94
Crystal system	Hexagonal	Tetragonal	Monoclinic
Space group	*P6/mmm* (No.191)	*I4/m* (No.87)	*C2/m* (No. 12)
a /Å	6.9195(5)	14.4398(13)	7.1962(10)
b /Å	6.9195(5)	14.4398(13)	14.7046(15)
c /Å	3.5596(3)	7.2843(9)	7.1852(9)
α /°	90	90	90
β /°	90	90	119.857(5)
γ /°	120	90	90
V/Å^3	147.60(2)	1518.8(3)	659.40(14)
Z	3	16	4
ρ_{calc}g/cm^3	2.834	4.536	2.8
μ/mm^{-1}	0.779	10.678	1.199
F(000)	120	1824	528
Theta range for data collection/°	5.895 to 27.428	1.995 to 27.538	2.770 to 27.522
Index ranges	-8≤ h ≤7, -8≤ k ≤8, -4≤ l ≤4	-18≤ h ≤18, -18≤ k ≤18, 9≤ l ≤9	-8≤ h ≤9, -18≤ k ≤18, -9≤ l ≤9
Reflections collected / unique	1240/89 [R(int) = 0.0415]	5623/942 [R(int) = 0.0672]	2884/798 [R(int) = 0.0574]
Data / restraints / parameters	89 / 0 / 11	942 / 12 / 77	798 / 0 / 69
Goodness-of-fit on F^2	1.349	1.252	1.078
Final *R* indices [I>2σ(I)][a]	R_1 = 0.0188, wR_2 = 0.0533	R_1 = 0.0525, wR_2 = 0.1317	R_1 = 0.0409, wR_2 = 0.1060
R indices (all data)[a]	R_1 = 0.0188, wR_2 = 0.0533	R_1 = 0.0584, wR_2 = 0.1352	R_1 = 0.0535, wR_2 = 0.1167
Largest diff. peak and hole / e·Å^{-3}	0.424 / -0.230	1.558 / -1.897	1.223 / -0.626

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$ and $wR_2=[\sum w(F_o^2-F_c^2)^2/\sum wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for AlF_3. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}(Å^2)$	BVS
Al(1)	5000	0	0	6(1)	3.177
F(1)	4225(3)	2112(2)	0	20(1)	1.029
F(2)	5000	0	5000	31(1)	1.060

Table S3. Bond lengths (Å) and angles (°) of AlF_3.

Atom	Bond	Atom	Bond
Al(1)-F(1)#1	1.7912(5)	Al(1)-F(1)	1.7912(5)
Al(1)-F(1)#2	1.7912(5)	Al(1)-F(2)#4	1.7798(15)
Al(1)-F(1)#3	1.7912(5)	Al(1)-F(2)	1.7798(15)
F(1)#2-Al(1)-F(1)	180	F(2)#4-Al(1)-F(1)	90
F(1)#2-Al(1)-F(1)#1	90.07(11)	F(2)-Al(1)-F(1)#2	90
F(1)-Al(1)-F(1)#3	90.07(11)	F(2)#4-Al(1)-F(1)#1	90
F(1)#3-Al(1)-F(1)#1	180.00(7)	F(2)-Al(1)-F(1)#3	90
F(1)-Al(1)-F(1)#1	89.93(11)	F(2)#4-Al(1)-F(1)#3	90
F(1)#2-Al(1)-F(1)#3	89.93(11)	F(2)-Al(1)-F(1)	90
F(2)-Al(1)-F(1)#1	90	F(2)#4-Al(1)-F(2)	180
F(2)#4-Al(1)-F(1)#2	90		

Symmetry transformations used to generate equivalent atoms:
#1 y,-x+y,-z #2 -x+1,-y,-z #3 -y+1,x-y,z
#4 x,y,z-1 #5 x-y,x,z #6 x,y,z+1

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $BaAlF_5$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}(Å^2)$	BVS
Ba(1)	564(1)	2222(1)	5000	19(1)	2.351
Ba(2)	752(1)	7580(1)	0	23(1)	2.322
Al(1)	0	5000	5000	28(2)	2.917
Al(2)	1775(4)	6636(4)	5000	28(1)	2.979
Al(3)	0	10000	2474(12)	27(2)	3.175
F(1)	669(9)	3913(8)	5000	38(3)	1.134
F(2)	0	5000	7500	14(2)	0.949
F(3)	1094(9)	5560(9)	5000	43(3)	1.150
F(4)	2499(7)	6077(7)	6700(13)	48(2)	1.005
F(5)	2489(10)	7641(9)	5000	47(3)	1.207
F(6)	1005(6)	7101(7)	3304(12)	45(2)	1.120
F(7)	483(6)	8880(6)	2563(16)	52(3)	1.004
F(8)	0	10000	0	79(11)	0.999
F(9)	0	10000	5000	79(11)	0.901

Table S5. Selected bond lengths(Å) and angles (°) of $BaAlF_5$.

Atom	Bond	Atom	Bond
Ba(1)-F(1)	2.447(12)	Al(1)-F(1)	1.843(11)
Ba(1)-F(4)#3	2.547(10)	Al(1)-F(1)#1	1.843(11)
Ba(1)-F(4)#4	2.547(10)	Al(1)-F(3)	1.774(12)
Ba(1)-F(5)#5	2.619(13)	Al(1)-F(3)#1	1.774(12)
Ba(1)-F(6)#6	2.760(9)	Al(1)-F(2)	1.8211(2)
Ba(1)-F(6)#1	2.760(9)	Al(1)-F(2)#1	1.8211(2)
Ba(1)-F(7)#6	2.823(10)	Al(2)-F(3)	1.839(13)
Ba(1)-F(7)#1	2.823(10)	Al(2)-F(4)	1.811(10)
Ba(2)-F(1)#8	2.803(13)	Al(2)-F(4)#12	1.811(10)
Ba(2)-F(3)#8	2.864(14)	Al(2)-F(5)	1.781(14)
Ba(2)-F(4)#8	2.919(10)	Al(2)-F(6)#12	1.792(10)
Ba(2)-F(4)#9	2.919(10)	Al(2)-F(6)	1.792(10)
Ba(2)-F(5)#10	2.559(15)	Al(3)-F(7)	1.763(9)
Ba(2)-F(6)	2.531(9)	Al(3)-F(7)#13	1.763(9)
Ba(2)-F(6)#11	2.531(9)	Al(3)-F(7)#14	1.763(9)
Ba(2)-F(7)#11	2.675(10)	Al(3)-F(7)#15	1.763(9)
Ba(2)-F(7)	2.675(10)	Al(3)-F(8)	1.802(9)
		Al(3)-F(9)	1.840(9)
F(1)#1-Al(1)-F(1)	180	F(6)#12-Al(2)-F(3)	89.1(5)
F(3)#1-Al(1)-F(1)#1	85.5(6)	F(6)-Al(2)-F(3)	89.1(5)
F(3)-Al(1)-F(1)	85.5(6)	F(6)-Al(2)-F(4)	175.2(6)
F(3)-Al(1)-F(1)#1	94.5(6)	F(6)#12-Al(2)-F(4)	93.1(4)
F(3)#1-Al(1)-F(1)	94.5(6)	F(6)-Al(2)-F(4)#12	93.1(4)
F(3)#1-Al(1)-F(3)	180	F(6)#12-Al(2)-F(4)#12	175.2(6)
F(3)#1-Al(1)-F(2)#1	90	F(6)#12-Al(2)-F(6)	87.2(6)
F(3)-Al(1)-F(2)	90	F(7)#13-Al(3)-F(7)	175.8(9)

F(3)-Al(1)-F(2)#1	90	F(7)#14-Al(3)-F(7)	89.92(4)
F(3)#1-Al(1)-F(2)	90	F(7)#15-Al(3)-F(7)#13	89.92(4)
F(2)-Al(1)-F(1)	90	F(7)#15-Al(3)-F(7)	89.92(4)
F(2)#1-Al(1)-F(1)	90	F(7)#14-Al(3)-F(7)#13	89.92(4)
F(2)-Al(1)-F(1)#1	90	F(7)#14-Al(3)-F(7)#15	175.8(9)
F(2)#1-Al(1)-F(1)#1	90	F(7)-Al(3)-F(8)	92.1(5)
F(2)#1-Al(1)-F(2)	180	F(7)#15-Al(3)-F(8)	92.1(5)
F(4)-Al(2)-F(3)	86.1(5)	F(7)#14-Al(3)-F(8)	92.1(5)
F(4)#12-Al(2)-F(3)	86.1(5)	F(7)#13-Al(3)-F(8)	92.1(5)
F(4)-Al(2)-F(4)#12	86.3(7)	F(7)#14-Al(3)-F(9)	87.9(5)
F(5)-Al(2)-F(3)	176.9(7)	F(7)#15-Al(3)-F(9)	87.9(5)
F(5)-Al(2)-F(4)	91.7(5)	F(7)#13-Al(3)-F(9)	87.9(5)
F(5)-Al(2)-F(4)#12	91.7(5)	F(7)-Al(3)-F(9)	87.9(5)
F(5)-Al(2)-F(6)	93.1(5)	F(8)-Al(3)-F(9)	180
F(5)-Al(2)-F(6)#12	93.1(5)		

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1 #2 -x,-y+1,-z #3 y-1/2,-x+1/2,-z+3/2
#4 y-1/2,-x+1/2,z-1/2 #5 -y+1,x,z #6 -x,-y+1,z
#7 -y+1,x,-z+1 #8 -y+1/2,x+1/2,z-1/2 #9 -y+1/2,x+1/2,-z+1/2
#10 -x+1/2,-y+3/2,-z+1/2 #11 x,y,-z #12 x,y,-z+1
#13 -x,-y+2,z #14 -y+1,x+1,z #15 y-1,-x+1,z
#16 -y+1/2,x+1/2,z+1/2 #17 y-1/2,-x+1/2,-z+1/2
#18 y,-x+1,-z+1 #19 -y,x+1,z #20 x,y+1,z
#21 -x,-y+2,-z #22 -x,-y+2,-z+1 #23 -y+1/2,x+1/2,-z+3/2

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Li_2KAl_2F_9$. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U_{eq}(Å^2)$	BVS
Li(1)	10000	7101(4)	5000	21(1)	0.911
Li(2)	5000	6971(4)	10000	17(1)	1.029
K(1)	2463(1)	5000	7459(1)	25(1)	0.836
Al(1)	7516(1)	6212(1)	7501(1)	8(1)	3.047
F(1)	5000	6421(1)	5000	20(1)	1.027
F(2)	10000	6037(1)	10000	23(1)	0.967
F(3)	7175(3)	5000	7006(3)	20(1)	0.967
F(4)	6077(2)	6111(1)	8894(2)	18(1)	1.031
F(5)	7686(2)	7419(1)	7766(2)	20(1)	0.918
F(6)	8928(2)	6221(1)	6071(2)	19(1)	1.001

Table S7. Selected bond lengths(Å) and angles (°) of $Li_2KAl_2F_9$.

Atom	Bond	Atom	Bond
Li(1)-F(1)#4	2.174(6)	K(1)-F(4)#6	2.8102(15)
Li(1)-F(5)#4	2.088(3)	K(1)-F(6)#12	2.8569(16)
Li(1)-F(5)#3	2.088(3)	K(1)-F(6)#13	2.8569(16)
Li(1)-F(6)#5	1.858(5)	K(1)-F(6)#14	2.8509(16)
Li(1)-F(6)	1.858(5)	K(1)-F(6)#1	2.8509(16)
Li(2)-F(4)	1.857(4)	Al(1)-F(1)	1.8337(7)
Li(2)-F(4)#9	1.857(4)	Al(1)-F(2)	1.8137(7)
Li(2)-F(5)#7	1.868(3)	Al(1)-F(3)	1.8102(8)
Li(2)-F(5)#8	1.868(3)	Al(1)-F(4)	1.7686(17)
K(1)-F(4)#11	2.7970(16)	Al(1)-F(5)	1.7828(17)
K(1)-F(4)	2.7970(16)	Al(1)-F(6)	1.7690(18)
K(1)-F(4)#9	2.8102(16)		
F(2)-Al(1)-F(1)	178.39(8)	F(5)-Al(1)-F(1)	85.40(8)
F(3)-Al(1)-F(1)	90.07(9)	F(5)-Al(1)-F(2)	93.09(8)
F(3)-Al(1)-F(2)	91.46(9)	F(5)-Al(1)-F(3)	175.32(8)
F(4)-Al(1)-F(1)	89.90(6)	F(6)-Al(1)-F(1)	90.12(6)
F(4)-Al(1)-F(2)	89.65(6)	F(6)-Al(1)-F(2)	90.45(6)
F(4)-Al(1)-F(3)	88.17(8)	F(6)-Al(1)-F(3)	87.34(8)
F(4)-Al(1)-F(5)	92.99(7)	F(6)-Al(1)-F(5)	91.49(7)
F(4)-Al(1)-F(6)	175.51(8)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 x+1,y,z #3 x+1/2,-y+3/2,z
#4 -x+3/2,-y+3/2,-z+1 #5 -x+2,y,-z+1 #6 -x+1,-y+1,-z+2
#7 -x+3/2,-y+3/2,-z+2 #8 x-1/2,-y+3/2,z #9 -x+1,y,-z+2
#10 -x,-y+1,-z+1 #11 x,-y+1,z #12 x-1,y,z
#13 x-1,-y+1,z #14 -x+1,y,-z+1 #15 -x+2,y,-z+2

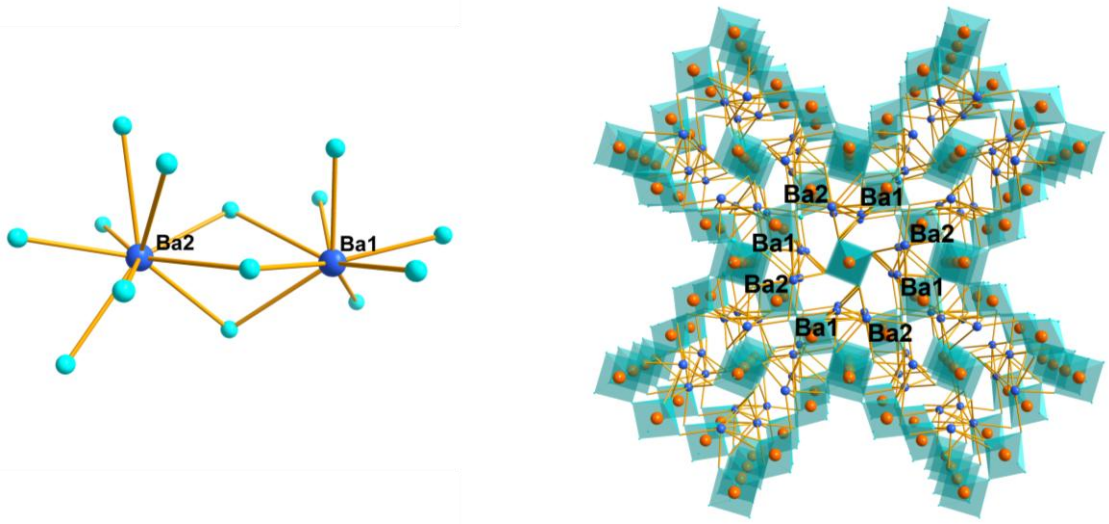

Figure S1. Ba atom coordination environment in the $BaAlF_5$ structure.

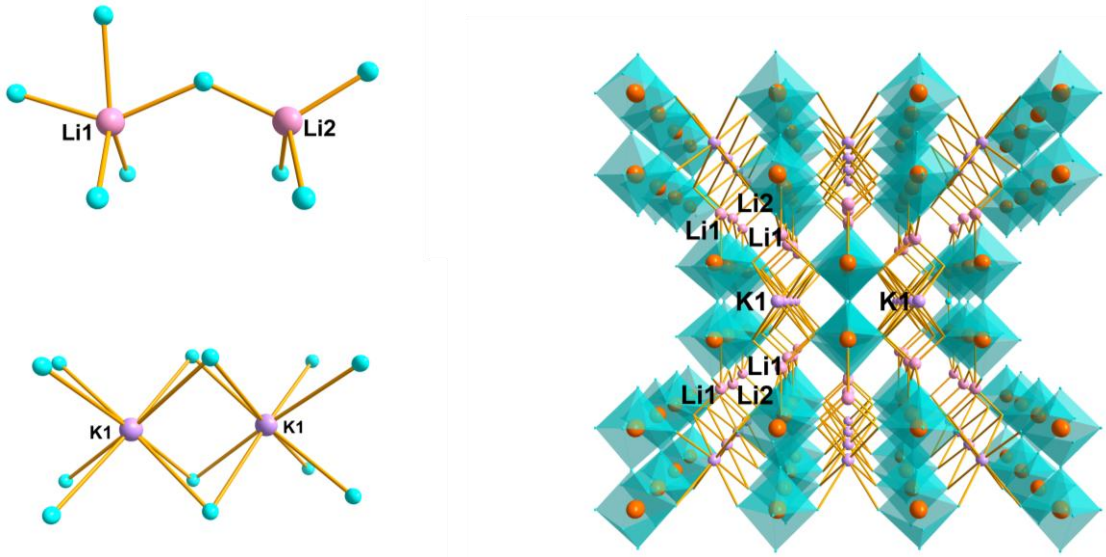

Figure S2. Li and K atom coordination environment in the $Li_2KAl_2F_9$ structure.

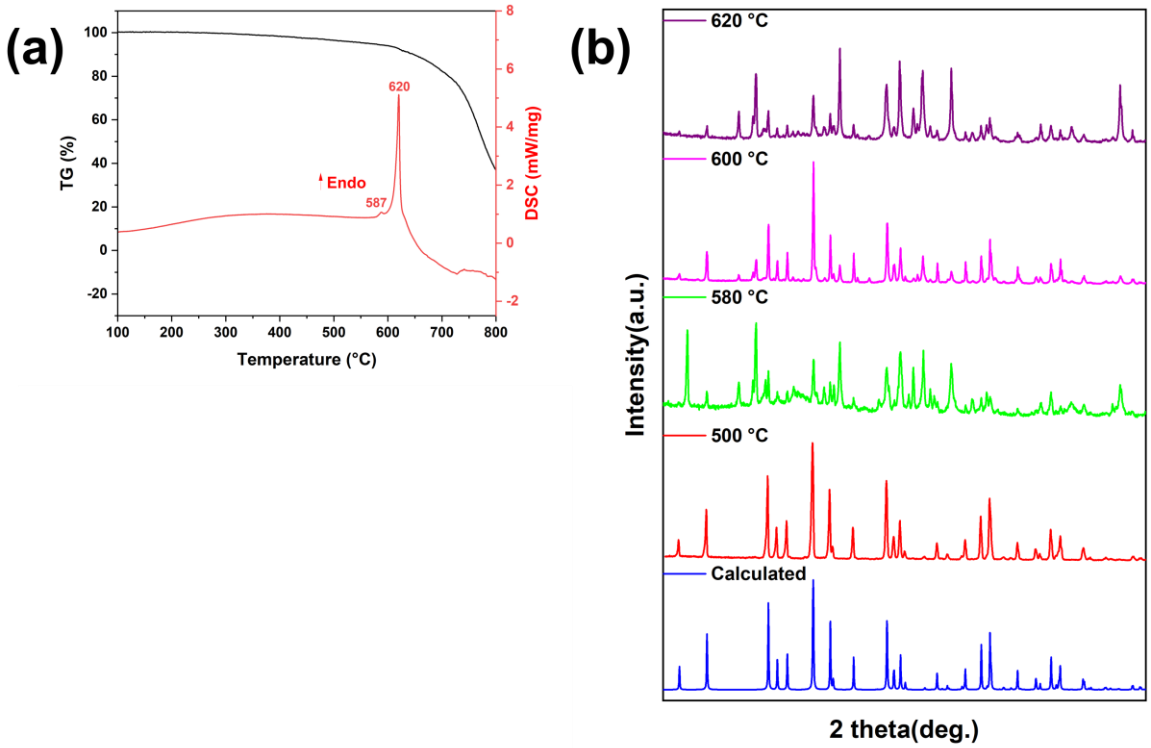

Figure. S3. (a) The TG and DSC curves of $Li_2KAl_2F_9$. (b) The calcination experiments.

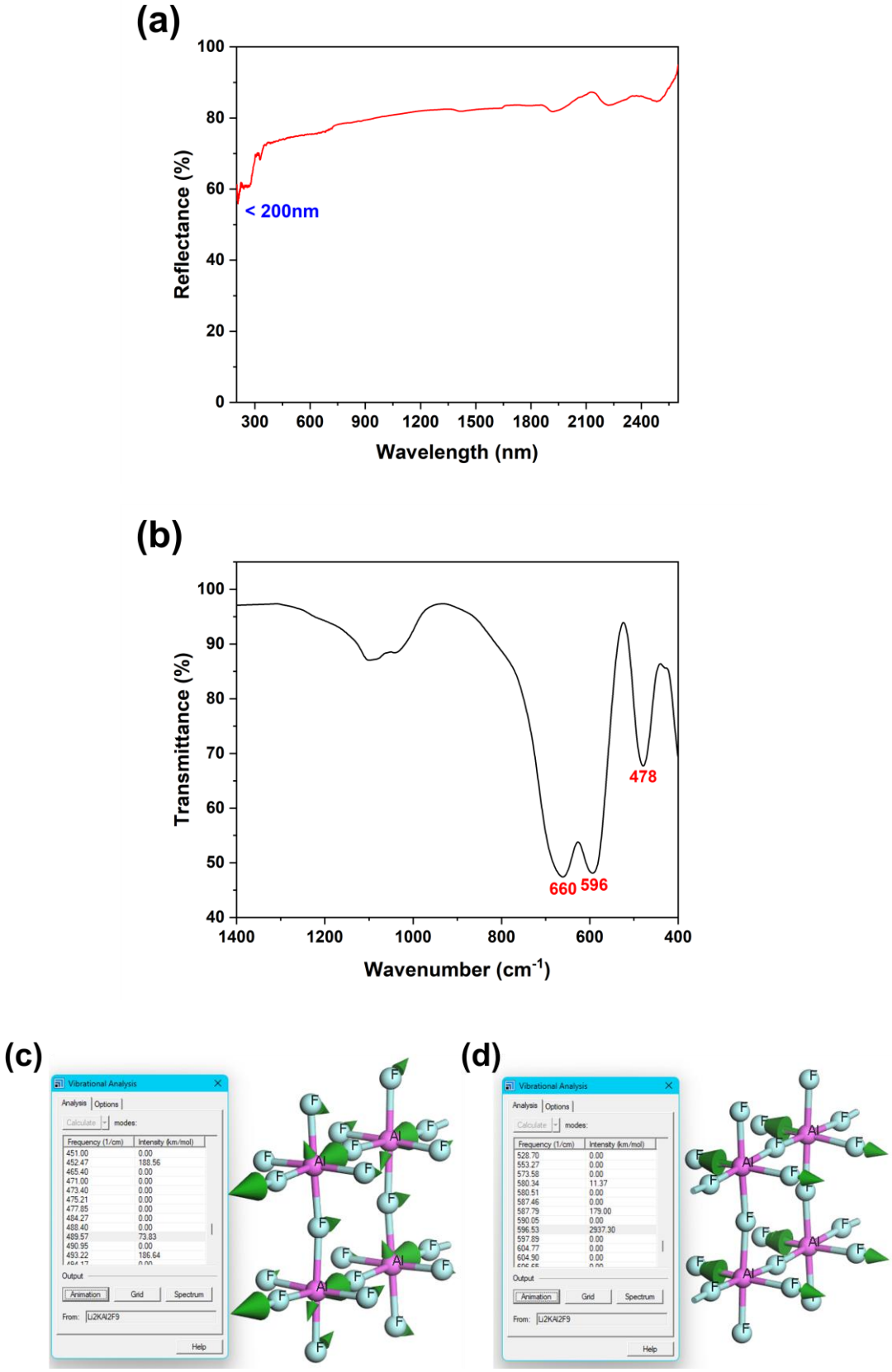

Figure. S4. (a) The UV-vis-NIR diffuse reflectance spectrum of $Li_2KAl_2F_9$. (b-d) The peaks at 660, 596 and 478 cm^{-1} could arise from the stretch-bend vibrations of the [AlF_6] units.

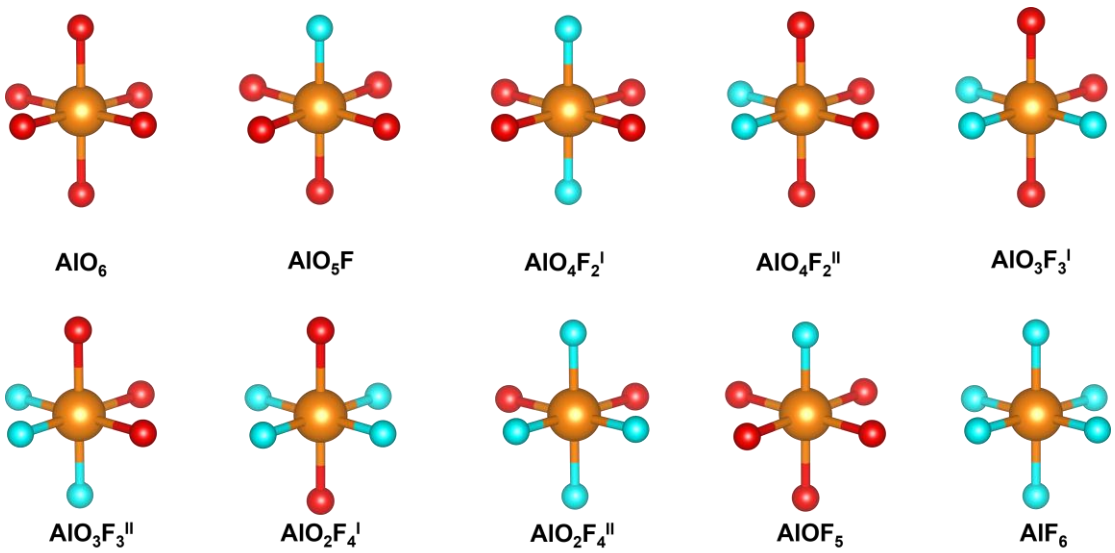

Figure S5. Geometric configuration of the available [AlO_mF_n] (m + n = 6) units. The orange, red, and blue atoms are Al, O, and F atoms, respectively.

Table S8. Polarizability anisotropy and HOMO-LUMO calculations of the experimental structure and theoretical model of $[AlO_mF_n]$ (m + n = 6) units.

Number	Cluster	Polarization anisotropy	HOMO-LOMO gap	ICSD code
1[a]	AlO_6	0.32	2.97	30538
2[a]	AlO_5F	7.14	2.69	68320
3[a]	$AlO_4F_2^{I}$	9.84	2.79	186579
4[a]	$AlO_4F_2^{II}$	2.44	2.69	186579
5[a]	$AlO_3F_3^{I}$	8.94	3.08	166958
6[a]	$AlO_3F_3^{II}$	9.74	2.27	79740
7[a]	$AlO_2F_4^{I}$	2.84	4.19	170410
8[a]	$AlO_2F_4^{II}$	4.23	3.54	79700
9[a]	$AlOF_5$	3.13	3.92	92303
10[a]	AlF_6	0.12	9.17	this work
11[b]	AlO_6	0.00	2.85	/
12[b]	AlO_5F	1.87	2.64	/
13[b]	$AlO_4F_2^{I}$	10.02	2.83	/
14[b]	$AlO_4F_2^{II}$	0.14	2.70	/
15[b]	$AlO_3F_3^{I}$	8.26	3.12	/
16[b]	$AlO_3F_3^{II}$	2.29	2.53	/
17[b]	$AlO_2F_4^{I}$	2.92	4.25	/
18[b]	$AlO_2F_4^{II}$	7.78	3.01	/
19[b]	$AlOF_5$	3.48	3.70	/
20[b]	AlF_6	0.00	9.20	/

[a]experimental structure and [b]theoretiacl model

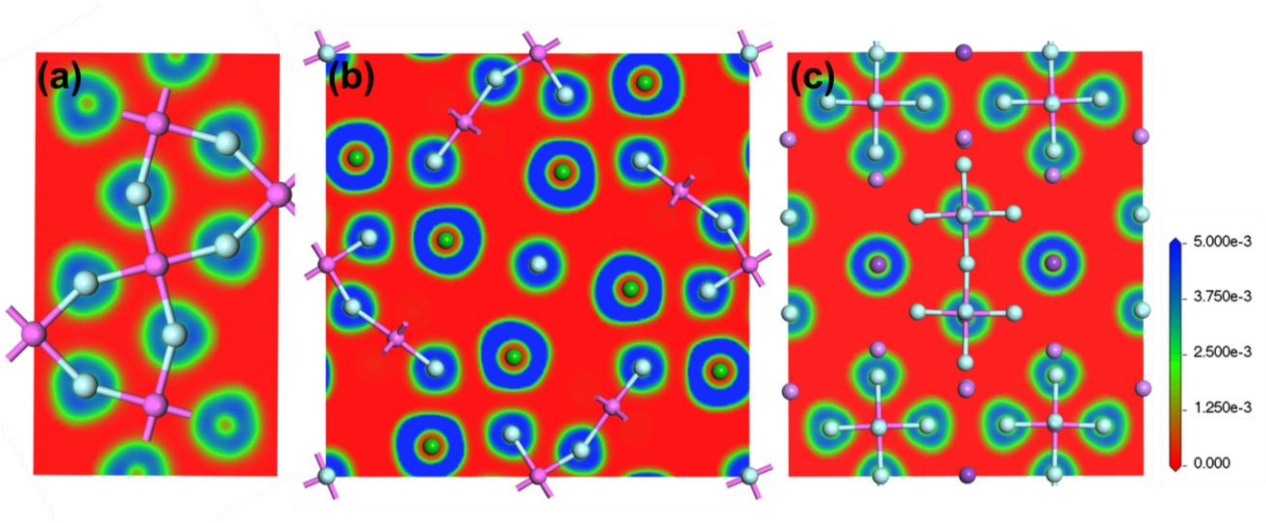

Figure S6. The electron localization function of (a) AlF_3, (b) $BaAlF_5$, and (c) $Li_2KAl_2F_9$.