Supplemental Materials for "Computational design of new DUV NLO fluorooxoborates with $[BO_3]$:$[BO_3F]$ = 2:1 via anionic framework dimensionality-fixed strategy"

Table S1. Basic parameters and E_{hull} of $CaB_6O_9F_2$-I and CaB_3O_5F~I-IV.

Structure	Space group	E_{hull} (eV/atom)
$CaB_6O_9F_2$-I	*C2*(no.5)	0.0094
CaB_3O_5F-I	$P2_1$(no.4)	0.0442
CaB_3O_5F-II	*Pc*(no.7)	0.0297
CaB_3O_5F-III	$P2_1$(no.4)	0.0250
CaB_3O_5F-IV	*Pc*(no.7)	0.0400

The structural rationality of $CaB_6O_9F_2$-I and CaB_3O_5F~I-IVare also evident from bond valence sum (BVS) calculations and global instability index (GII). Global instability index (GII) with well determined structures is usually < 0.1 valence unit (v.u.), 0.1< GII < 0.2 v.u. indicating a strained structure, while structures with GII > 0.2 v.u. are uncommon and be considered unstable. The BVS and GII values (Tables S2) indicate that the coordination of atoms in unit cell of $CaB_6O_9F_2$-I and CaB_3O_5F-I~IVare correct and feasible.

Table S2-I. Crystallographic structural data of $CaB_6O_9F_2$-I.

$CaB_6O_9F_2$-I (*C*2)					
Cell parameters					
a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
7.9355	8.9531	10.6472	90.0000	141.0695	90.0000
Fractional coordinates					
Atoms	*x/a*		*y/b*		*z/c*
Ca1	0.30540		0.69460		0.50000
B1	0.75681		0.97200		0.26955
B2	0.02800		0.24319		0.73045
B3	0.12090		0.22625		0.36392
B4	0.77375		0.87910		0.63608
B5	0.22952		0.45388		0.05148
B6	0.54612		0.77048		0.94852
O1	0.89811		0.16519		0.29302
O2	0.83481		0.10189		0.70698
O3	0.09898		0.31245		0.92247
O4	0.68755		0.90102		0.07753
O5	0.24106		0.40912		0.25136
O6	0.59088		0.75894		0.74864
O7	0.15542		0.31721		0.57301
O8	0.68279		0.84458		0.42699
O9	0.34568		0.65432		0.00000
F1	0.97257		0.75567		0.64907
F2	0.24433		0.02743		0.35093
Bond valence sum (BVS)					GII
Ca1	1.8976	B1	3.0334		0.083
B2	3.0325	B3	2.9819		
B4	2.9833	B5	3.0435		
B6	3.0454	O1	-1.9796		
O2	-1.9796	O3	-2.0550		
O4	-2.0568	O5	-2.1023		

O6	-2.1022	O7	-2.0267	
O8	-2.0269	O9	-1.9844	
F1	-0.8524	F2	-0.8522	

Table S2-II. Crystallographic structural data of CaB_3O_5F-I.

CaB_3O_5F-I ($P2_1$)					
Cell parameters					
a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
4.5599	8.7793	6.6902	90.0000	96.9681	90.0000
Fractional coordinates					
Atoms	*x/a*		*y/b*		*z/c*
Ca1	0.1728		0.0384		0.1129
B1	0.0612		0.0199		0.0539
B2	0.1694		0.0300		0.0457
B3	0.0854		0.0252		0.0036
O1	0.1255		0.0262		0.0653
O2	0.1491		0.0312		0.0151
O3	0.0124		0.0326		0.0578
O4	0.0577		0.0138		0.0225
O5	0.0615		0.0309		0.1262
F1	0.0496		0.0042		0.0707
Bond valence sum (BVS)					GII
Ca1	1.8937	B1	3.0145		
B2	3.0020	B3	2.9651		
O1	-2.0796	O2	-2.0448		0.084
O3	-1.8824	O4	-1.9885		
O5	-1.8262	F1	-0.9284		

Table S2-III. Crystallographic structural data of CaB_3O_5F-II.

CaB_3O_5F-II (Pc)					
Cell parameters					
a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
5.9346	5.5199	10.6694	90.0000	133.4949	90.0000
Fractional coordinates					
Atoms	*x/a*		*y/b*		*z/c*
Ca1	- 0.0464		- 0.1625		0.0027
B1	0.1980		- 0.0261		0.0828
B2	- 0.0946		- 0.0614		0.0149
B3	0.1516		- 0.0781		0.0854
O1	0.2012		- 0.1792		0.0746

O2	- 0.0493		- 0.0639	0.0311
O3	- 0.1351		- 0.0896	0.0075
O4	0.1561		- 0.0549	0.0752
O5	- 0.0974		- 0.0453	0.0615
F1	0.2948		- 0.0473	0.0883
	Bond valence sum (BVS)			GII
Ca1	1.7757	B1	2.9656	
B2	2.9784	B3	2.9790	
O1	-1.8722	O2	-2.0405	0.082
O3	-1.8566	O4	-1.9508	
O5	-2.0475	F1	-0.9113	

Table S2-IV. Crystallographic structural data of CaB_3O_5F-III.

CaB_3O_5F-III ($P2_1$)					
Cell parameters					
a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
5.3192	6.8636	6.8982	90.0000	110.0409	90.0000
Fractional coordinates					
Atoms	*x/a*		*y/b*		*z/c*
Ca1	0.1061		0.0425		0.1365
B1	0.1353		0.0148		0.0558
B2	0.0012		0.0847		0.0369
B3	0.1068		0.1329		0.0899
O1	0.1820		0.0184		0.0792
O2	0.1463		0.0842		0.0138
O3	0.1065		0.0405		0.0450
O4	0.1036		0.1373		0.0609
O5	0.1405		0.0039		0.1125
F1	0.0424		0.0781		0.1164
	Bond valence sum (BVS)				GII
Ca1	1.8281	B1	2.9843		
B2	2.9562	B3	2.9736		
O1	-1.8958	O2	-1.9105		0.084
O3	-2.0711	O4	-1.9382		
O5	-1.9642	F1	-0.9624		

Table S2-V. Crystallographic structural data of CaB_3O_5F-IV.

CaB_3O_5F-IV (*P*c)					
Cell parameters					
a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)
5.9639	9.2592	4.8890	90.0000	101.0361	90.0000
Fractional coordinates					
Atoms	*x/a*		*y/b*		*z/c*
Ca1	0.1029		0.0909		0.1705
B1	0.0627		0.0906		0.0565
B2	0.1407		0.0766		0.1939
B3	0.0071		0.0798		0.0892
O1	0.0444		0.0887		0.0008
O2	0.1574		0.0789		0.1362
O3	0.0464		0.0835		0.0993
O4	0.0961		0.0982		0.0706
O5	0.1561		0.0785		0.0328
F1	0.0310		0.0618		0.1983
Bond valence sum (BVS)					GII
Ca1	1.9403	B1	2.9794		
B2	2.8599	B3	2.8327		
O1	-2.0341	O2	-1.9463		0.092
O3	-2.0830	O4	-1.9246		
O5	-1.8904	F1	-0.9340		

Table S3-I. Bond lengths (Å) and angles (°) for $CaB_6O_9F_2$-I.

B(2)-O(1)	1.3488	B(4)-O(8)	1.4837
B(1)-O(4)	1.3746	B(5)-O(3)	1.3478
B(1)-O(8)	1.3778	B(5)-O(5)	1.3759
B(2)-O(2)	1.3492	B(5)-O(9)	1.3739
B(2)-O(3)	1.3746	B(6)-O(4)	1.3472
B(2)-O(7)	1.3779	B(6)-O(6)	1.3759
B(3)-F(2)	1.4813	B(6)-O(9)	1.3739
B(3)-O(1)	1.4028	Ca(1)-F(1)	2.3261
B(3)-O(5)	1.4799	Ca(1)-F(2)	2.3262
B(3)-O(7)	1.4837	Ca(1)-O(5)	2.3341
B(4)-F(1)	1.4812	Ca(1)-O(6)	2.3341
B(4)-O(2)	1.4023	Ca(1)-O(7)	2.4029
B(4)-O(6)	1.4799	Ca(1)-O(8)	2.4029
O(1)-B(1)-O(4)	117.2362	O(4)-B(1)-O(8)	119.5199
O(8)-B(1)-O(1)	123.2400	F(1)-B(4)-O(2)	109.3331
O(8)-B(4)-F(1)	106.2333	O(2)-B(4)-F(1)	109.3331
O(6)-B(4)-O(8)	101.9472	O(6)-B(6)-O(9)	115.5202
O(9)-B(6)-O(4)	124.1534	O(4)-B(6)-O(6)	120.1893
O(3)-B(5)-O(9)	124.1534	O(9)-B(5)-O(5)	115.5203
O(5)-B(5)-O(3)	120.1893	O(5)-B(3)-F(2)	108.8772
F(2)-B(3)-O(7)	106.2333	O(7)-B(3)-O(1)	117.0522
O(7)-B(2)-O(3)	119.5199	O(3)-B(2)-O(2)	117.2362
O(2)-B(2)-O(7)	123.2400		

Table S3-II. Bond lengths (Å) and angles (°) for CaB_3O_5F-I.

B(1)-O(3)	1.4339	Ca(1)-O(5)	2.5259
B(1)-O(1)	1.4575	Ca(1)-O(1)	2.4268
B(1)-O(4)	1.4769	Ca(1)-O(2)	2.4875
B(1)-F(1)	1.4529	Ca(1)-O(4)	2.5834
B(2)-O(2)	1.3846	Ca(1)-O(5)	2.3261
B(2)-O(1)	1.3712	Ca(1)-F(1)	2.3243
B(2)-O(3)	1.3569		
B(3)-O(2)	1.4373		
B(3)-O(4)	1.3907		

B(3)-O(5)	1.3202		
O(3)-B(1)-F(1)	109.8449	O(2)-B(3)-O(4)	114.6244
F(1)-B(1)-O(1)	107.6098	O(2)-B(3)-O(5)	116.5123
O(1)-B(1)-O(4)	112.0899	O(4)-B(3)-O(5)	128.8558
O(3)-B(1)-O(4)	112.1010		
O(1)-B(2)-O(3)	116.9338		
O(3)-B(2)-O(2)	123.1575		
O(2)-B(2)-O(1)	119.9053		

Table S3-III. Bond lengths (Å) and angles (°) for CaB_3O_5F-II.

B(1)-O(1)	1.3246	Ca(1)-O(1)	2.3588
B(1)-O(6)	1.3916	Ca(1)-O(5)	2.3136
B(1)-O(9)	1.4157	Ca(1)-O(2)	2.4608
B(2)-O(2)	1.3799	Ca(1)-O(6)	2.5174
B(2)-O(5)	1.3534	Ca(1)-O(9)	2.5143
B(2)-O(9)	1.3887	Ca(1)-F(1)	2.2636
B(3)-O(6)	1.4634		
B(3)-O(2)	1.4531		
B(3)-O(5)	1.4499		
B(3)-F(1)	1.4754		
O(6)-B(1)-O(1)	122.5140	O(2)-B(3)-O(5)	108.9081
O(1)-B(1)-O(9)	118.5213	O(5)-B(3)-F(1)	106.5286
O(9)-B(1)-O(6)	118.9394	F(1)-B(3)-O(6)	106.5290
O(9)-B(2)-O(5)	120.0296		
O(5)-B(2)-O(2)	123.3818		
O(2)-B(2)-O(9)	116.5878		
O(6)-B(3)-O(2)	113.6844		

Table S3-IV. Bond lengths (Å) and angles (°) for CaB_3O_5F-III.

B(1)-O(4)	1.4827	Ca(1)-O(5)	2.5132
B(1)-O(1)	1.4167	Ca(1)-O(2)	2.3354
B(1)-O(3)	1.4520	Ca(1)-O(1)	2.2859
B(1)-F(1)	1.4971	Ca(1)-O(3)	2.5409
B(2)-O(5)	1.4419	Ca(1)-O(4)	2.5794
B(2)-O(1)	1.3666	Ca(1)-F(1)	2.4071

B(2)-O(2)	1.3295	Ca(1)-F(1)	2.4610
B(3)-O(3)	1.3509		
B(3)-O(4)	1.3682		
B(3)-O(5)	1.4058		
O(1)-B(1)-F(1)	108.2616	O(5)-B(3)-O(3)	114.7298
F(1)-B(1)-O(3)	101.0400	O(3)-B(3)-O(4)	126.6769
O(3)-B(1)-O(4)	112.0450	O(4)-B(3)-O(5)	118.5734
O(4)-B(1)-O(1)	114.4109		
O(1)-B(2)-O(2)	125.2954		
O(1)-B(2)-O(5)	115.1986		
O(5)-B(2)-O(2)	119.5000		

Table S3-V. Bond lengths (Å) and angles (°) for CaB_3O_5F-IV.

B(1)-O(1)	1.3754	Ca(1)-O(1)	2.3914
B(1)-O(3)	1.4041	Ca(1)-O(2)	2.4754
B(1)-O(4)	1.3436	Ca(1)-O(3)	2.4581
B(2)-O(5)	1.5153	Ca(1)-O(4)	2.4351
B(2)-O(1)	1.4882	Ca(1)-O(4)	2.6337
B(2)-O(2)	1.4923	Ca(1)-O(4)	2.3056
B(2)-F(1)	1.3954	Ca(1)-O(5)	2.4699
B(3)-O(3)	1.4086		
B(3)-O(2)	1.3812		
B(3)-O(5)	1.3874		
O(1)-B(1)-O(4)	122.1087	O(3)-B(3)-O(5)	117.2583
O(4)-B(1)-O(3)	119.7574	O(5)-B(3)-O(2)	125.5862
O(3)-B(1)-O(1)	118.0746	O(2)-B(3)-O(3)	116.9749
O(1)-B(2)-F(1)	109.4056		
F(1)-B(2)-O(2)	110.7169		
O(2)-B(2)-O(5)	107.6461		
O(5)-B(2)-O(1)	107.9252		

Table S4. Comparison of key NLO properties between the predicted structures and representative UV/DUV materials.

Compounds	E_g (eV)	Δn	Max. $\lvert d_{ij}\rvert$ (pm V-1)	λ_{PM} (nm)
$CaB_6O_9F_2$-I	7.632	0.101@1064 nm	0.235	162
CaB_3O_5F-IV	6.979	0.085@1064 nm	1.124	192
KBBF	8.45	0.088@1064 nm	0.47	161
β-BBO	6.56	0.113@1064 nm	1.60	205
LBO	7.75	0.04@400 nm	1.05	276

Table S5. $\Delta\rho^b$, group contribution and corresponding birefringence of $CaB_6O_9F_2$-I and CaB_3O_5F~I-IV.

Structures	Groups	$\Delta\rho^b$ ($\times10^{-2}$)	Group contribution	Birefringence
$CaB_6O_9F_2$-I	$[CaO_4F_2]$	0.0811	2.87%	0.101
	$[BO_3]$	2.4466	86.67%	
	$[BO_3F]$	0.2953	2.82%	
CaB_3O_5F-I	$[CaO_5F]$	0.0731	4.04%	0.081
	$[BO_3]$	1.6725	92.34%	
	$[BO_3F]$	0.0656	3.62%	
CaB_3O_5F-II	$[CaO_5F]$	0.1462	9.93%	0.065
	$[BO_3]$	1.1882	80.67%	
	$[BO_3F]$	0.1385	9.40%	
CaB_3O_5F-III	$[CaO_5F_2]$	-0.0880	-5.16%	0.052
	$[BO_3]$	1.7103	99.95%	
	$[BO_3F]$	0.0892	5.21%	
CaB_3O_5F-IV	$[CaO_7]$	0.0621	3.42%	0.085
	$[BO_3]$	1.8065	99.43%	
	$[BO_3F]$	-0.0520	-2.84%	

Table S6. Contributions of the respective groups to birefringence and SHG coefficients in $CaB_6O_9F_2$-I and CaB_3O_5F-I~IV.

Structures		Δn	$\lvert d_{ij}\rvert$
$CaB_6O_9F_2$-I ($C2$)	[B-O/F] anionic framework	0.098	0.239
	Ca^{2+}	0.007	0.012
CaB_3O_5F-I ($P2_1$)	[B-O/F] anionic framework	0.065	0.345
	Ca^{2+}	0.01	0.091
CaB_3O_5F-II (Pc)	[B-O/F] anionic framework	0.041	0.712
	Ca^{2+}	0.018	0.138
CaB_3O_5F-III($P2_1$)	[B-O/F] anionic framework	0.057	0.484
	Ca^{2+}	0.002	0.072
CaB_3O_5F-IV (Pc)	[B-O/F] anionic framework	0.067	0.889
	Ca^{2+}	0.006	0.042

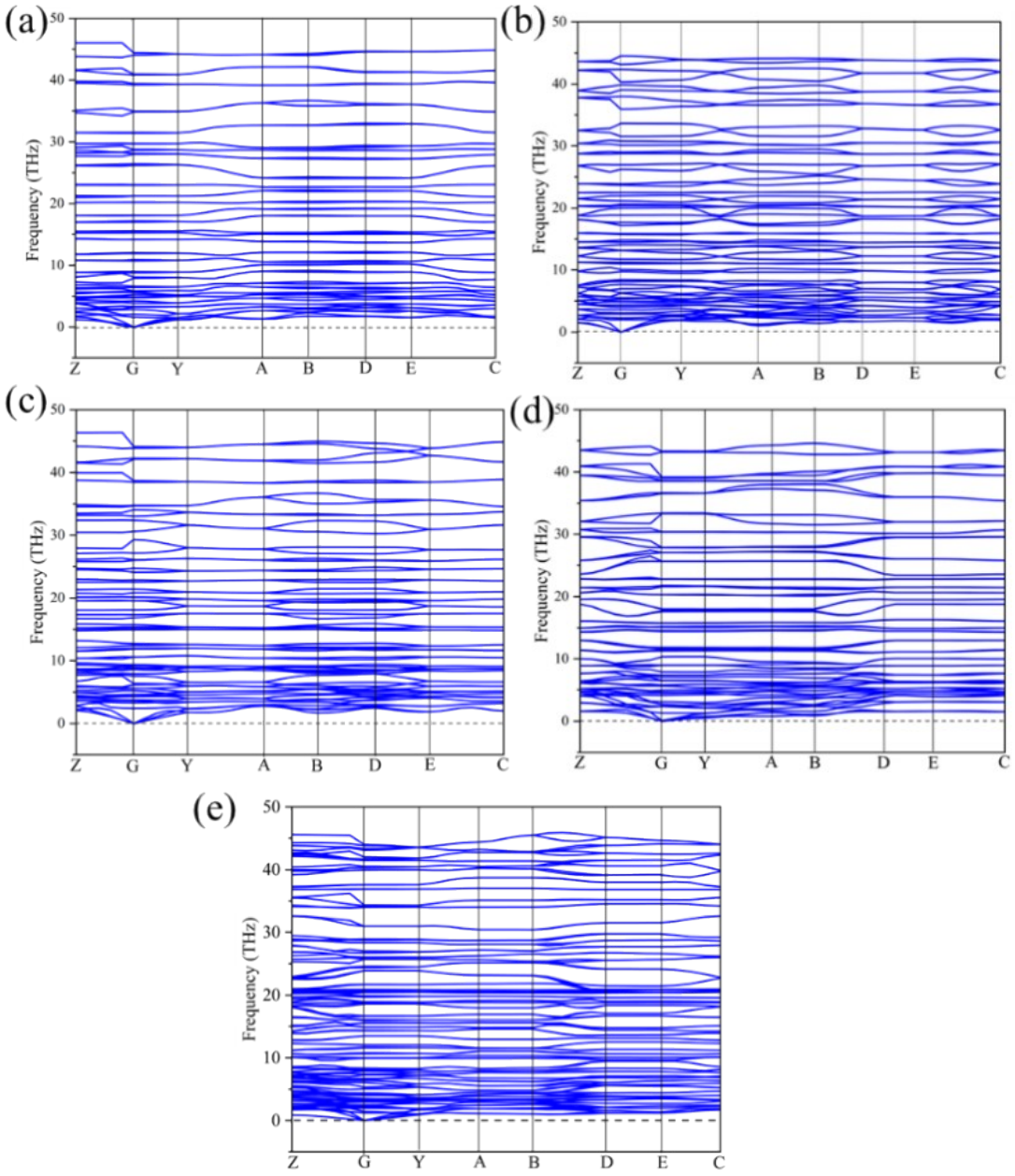

Figure S1. Phonon spectra of (a) CaB_3O_5F-I, (b) CaB_3O_5F-II, (c) CaB_3O_5F-III, (d) CaB_3O_5F-IV, and (e) $CaB_6O_9F_2$-I.

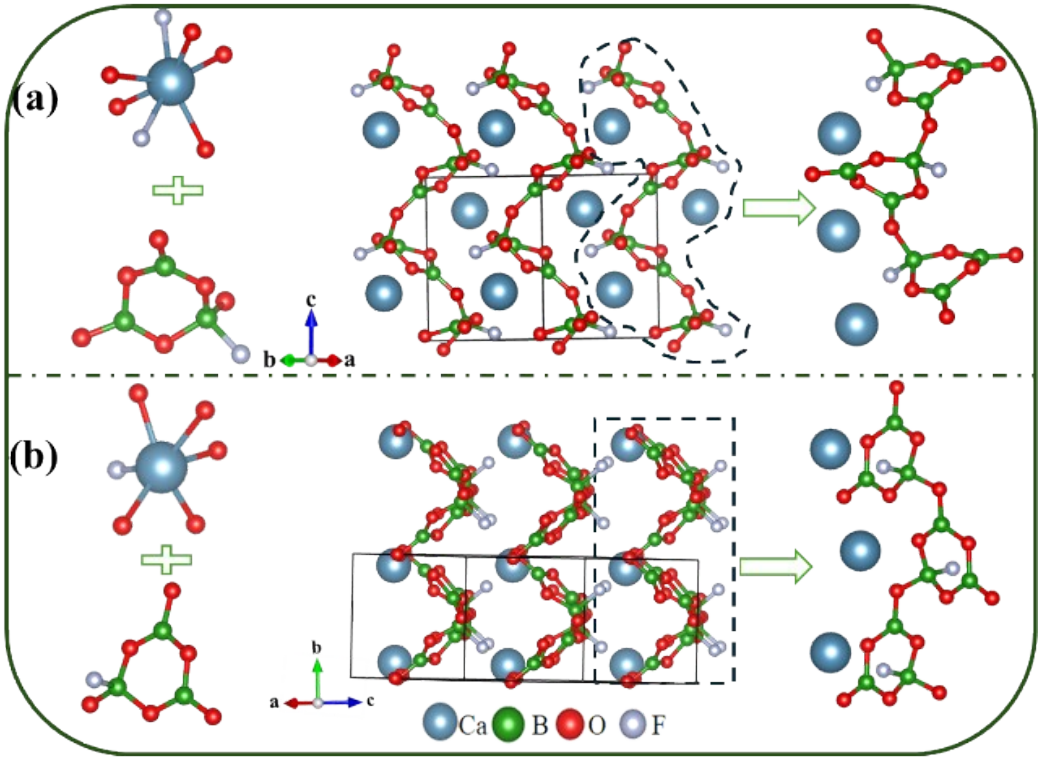

Figure S2. Fluorooxoborates structures of (a) CaB_3O_5F-III (b) CaB_3O_5F-II.

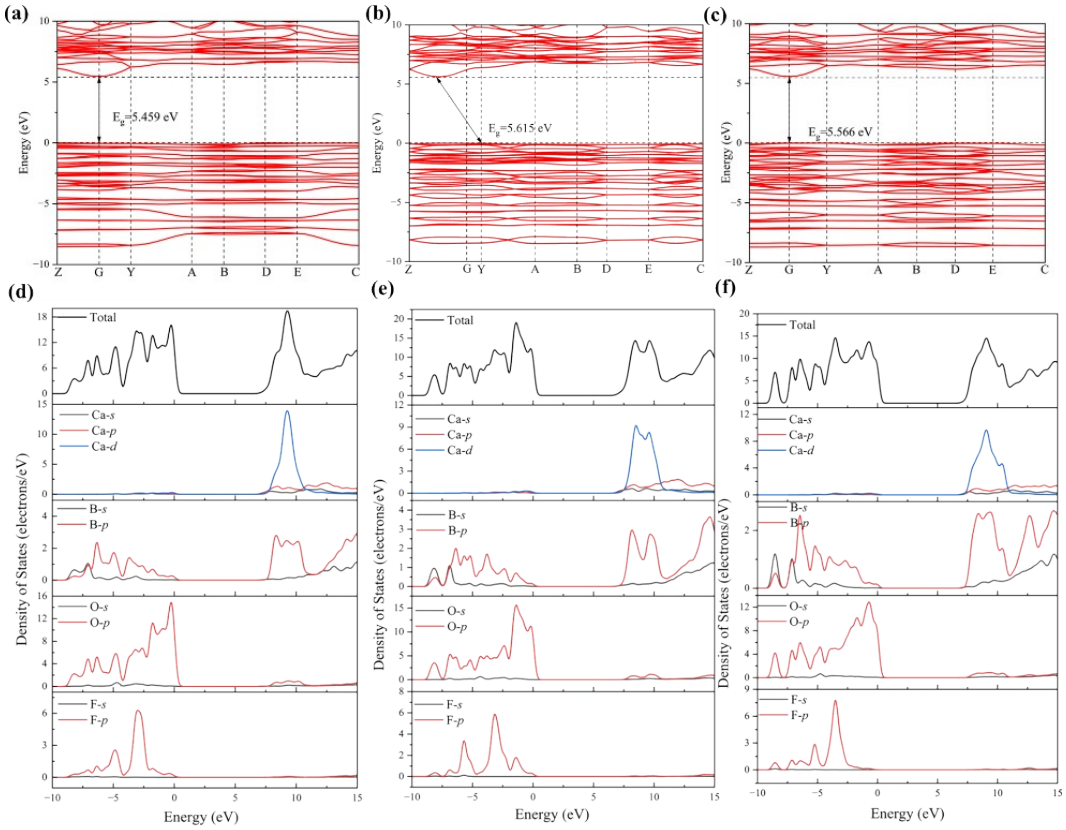

Figure S3. Band structure and Density of states for CaB_3O_5F~I-III. (a, d) CaB_3O_5F-I, (b, e) CaB_3O_5F-II, (c, f) CaB_3O_5F-III.

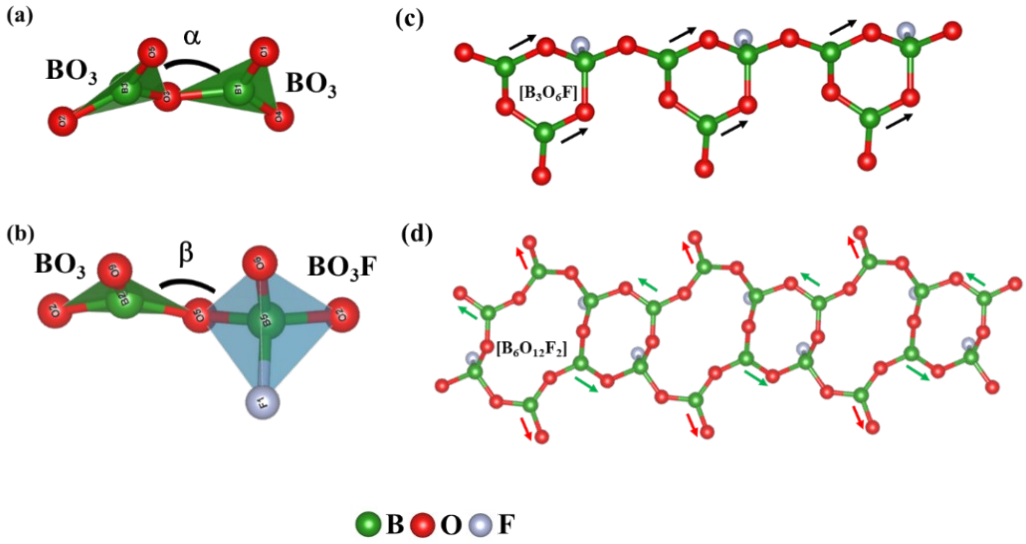

Figure S4. (a) Dihedral angles α between adjacent BO_3 groups, (b) the dihedral angles β between adjacent BO_3 and BO_3F groups, the orientation of BO_3 in the basic building block (c) CaB_3O_5F-IV (d) $CaB_6O_9F_2$-I.