Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information for:

Lone Pair Electron Effect Induced Differences in Linear and Nonlinear Optical Properties of Bismuth Borates

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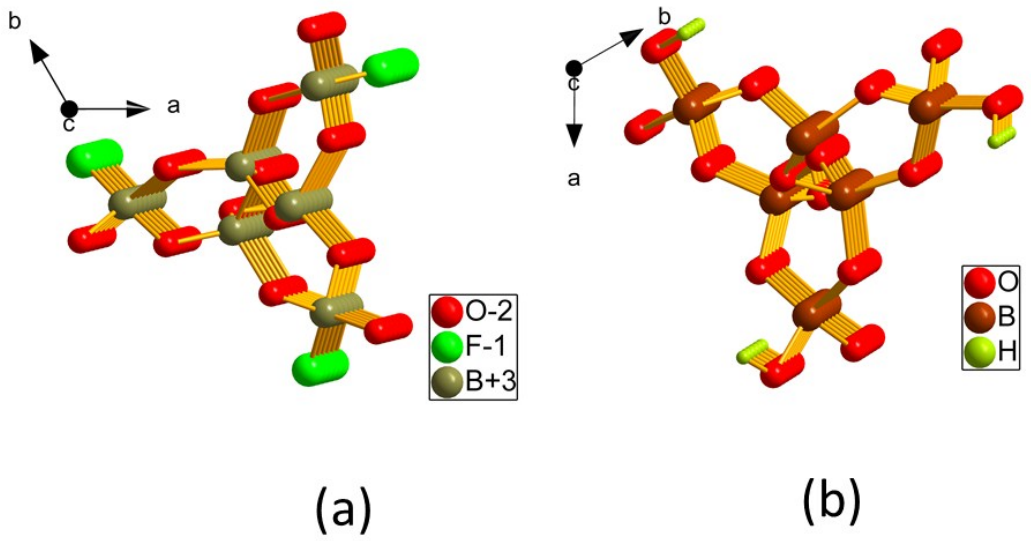

Fig. S1 Anion structure of (a) BiB_2O_4F, (b) $BiB_2O_4(OH)$

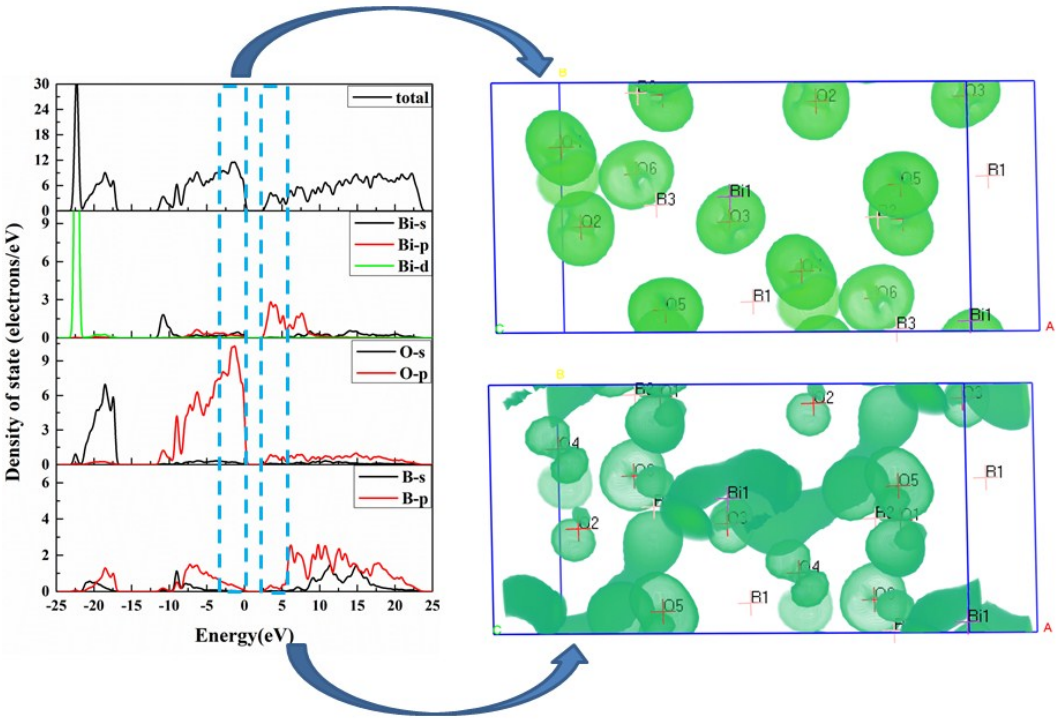

Fig. S2 PDOS/DOS as well as the orbital near the Fermi level of α-BiB_3O_6

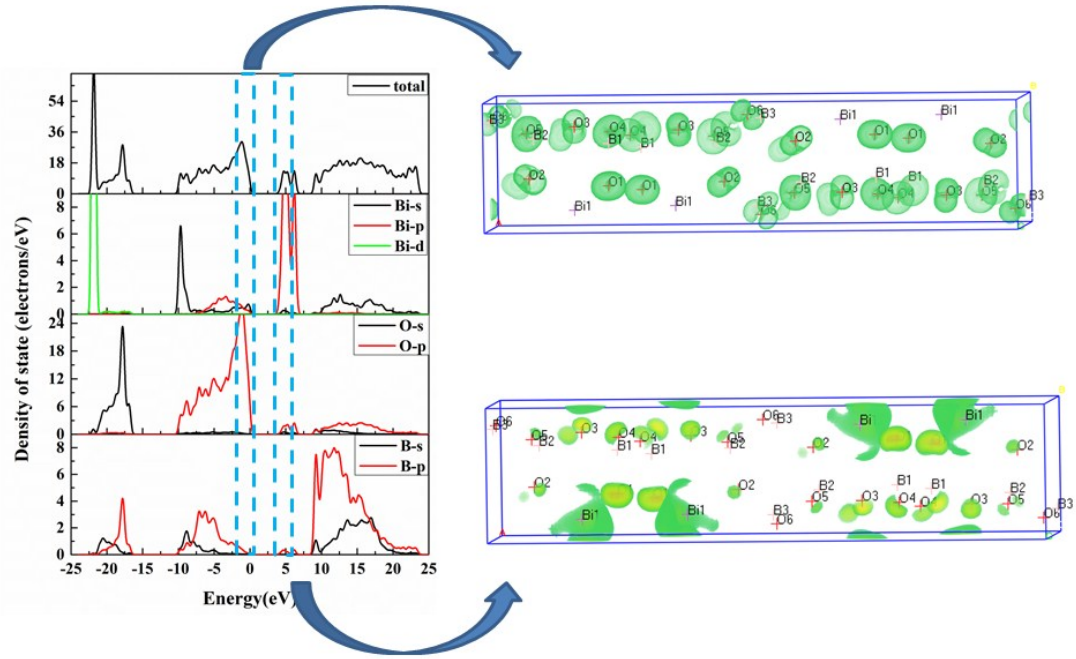

Fig. S3 PDOS/DOS as well as the orbital near the Fermi level of δ-BiB_3O_6

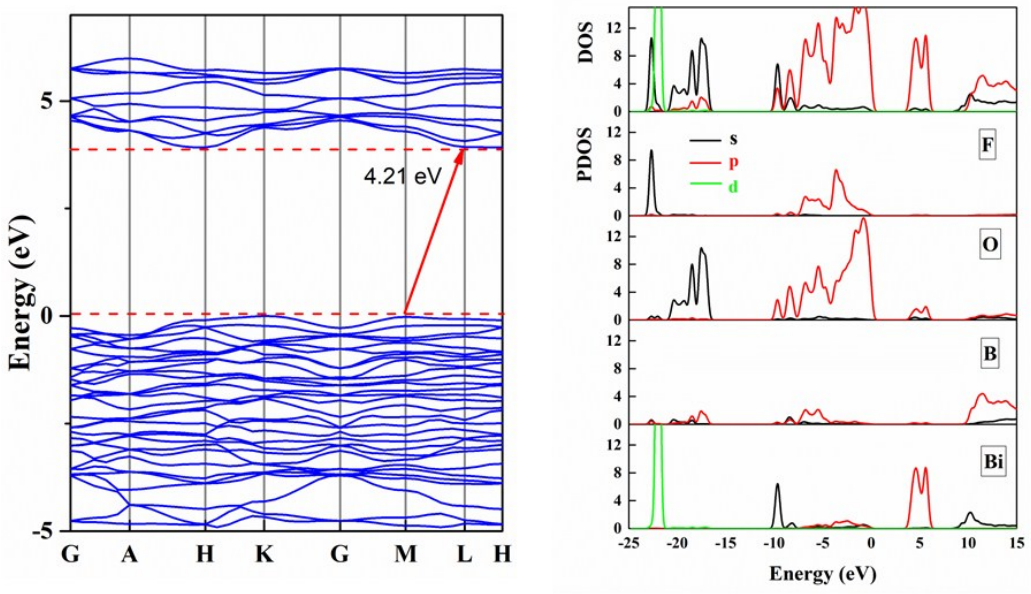

Fig. S4 Electronic band structure and DOS/PDOS of BiB_2O_4F

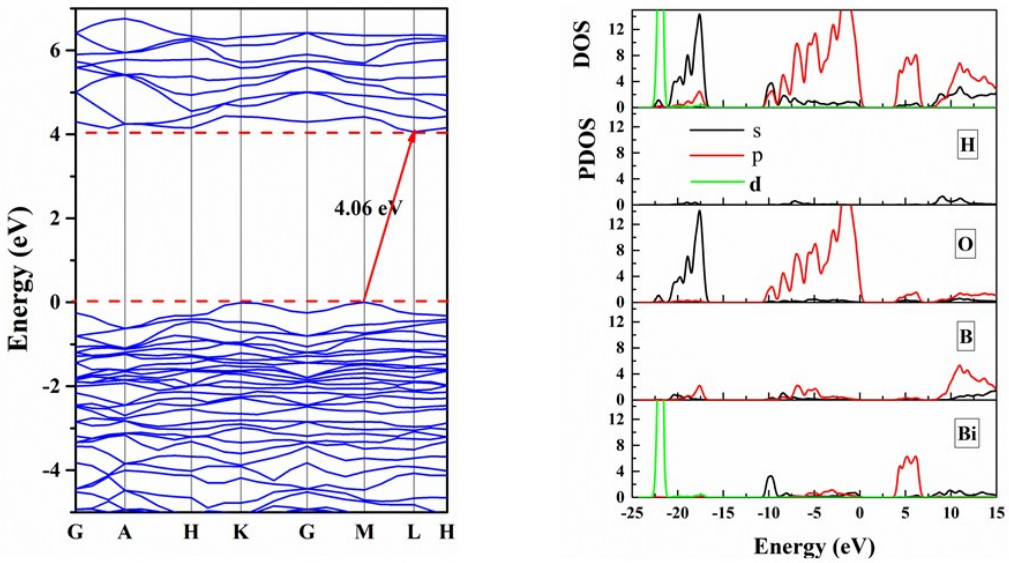

Fig. S5 Electronic band structure and DOS/PDOS of $BiB_2O_4(OH)$

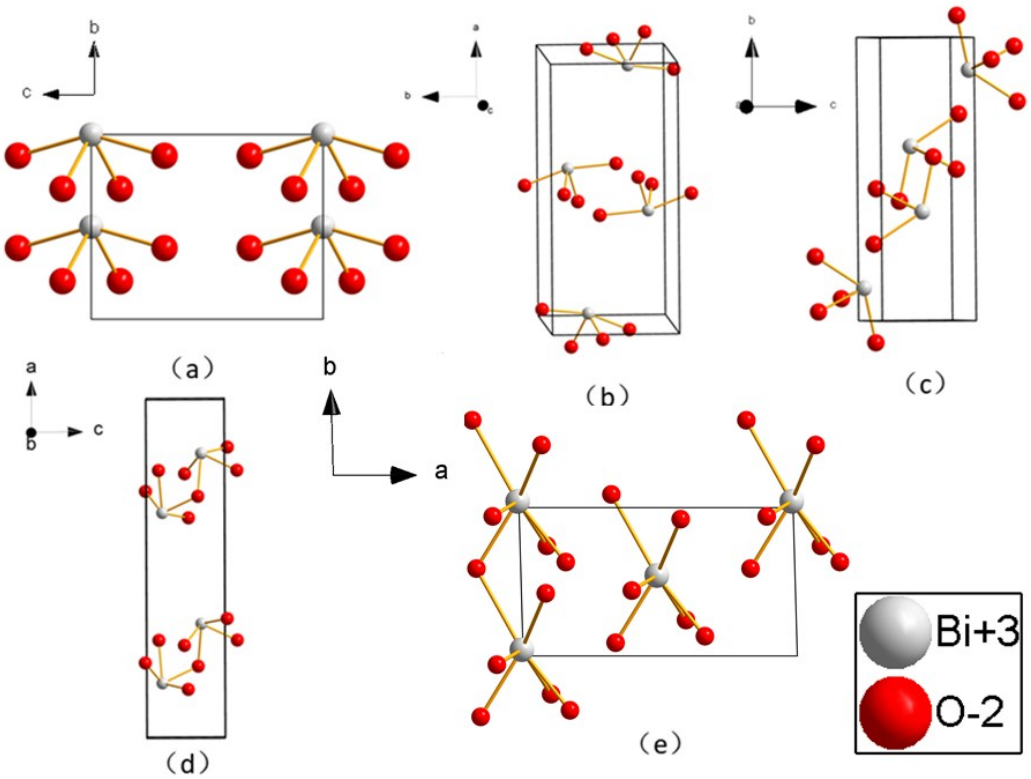

Fig. S6 The arrangement of bismuth oxygen polyhedra (a) α-BiB_3O_6, (b) β-BiB_3O_6, (c) γ-BiB_3O_6, (d) δ-BiB_3O_6, (e) ε-BiB_3O_6

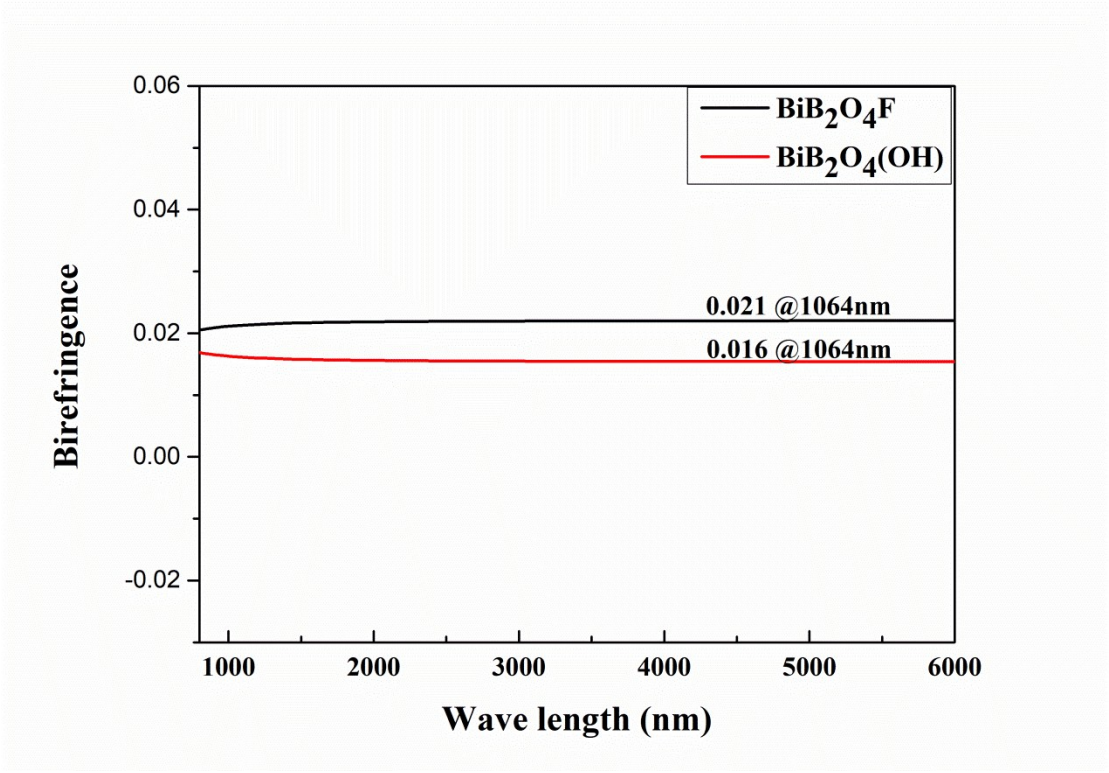

Fig. S7 Birefringence of BiB_2O_4F and $BiB_2O_4(OH)$

Table S1 Classification of BIBO and BiB_2O_4F and $BiB_2O_4(OH)$ according to the type of B-O structure

compound	α-BiB_3O_6	β-BiB_3O_6	γ-BiB_3O_6	δ-BiB_3O_6	ε-BiB_3O_6	BiB_2O_4F	$BiB_2O_4(OH)$
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic	trigonal	trigonal
Space group	C2	$P2_1/n$	$P2_1/n$	$Pna2_1$	C1	$P3_2$	$P3_1$
structure of B-O	Layered	Layered	3D	3D	Layered	chain	chain
FBB	B_3O_8	B_3O_8	B_3O_9	B_3O_{10}	B_3O_8	B_3O_8F	B_3O_9H
a(Å)	7.116	14.1664	8.4992	18.4480	7.4781	6.7147	6.6221
b(Å)	4.993	6.7514	11.7093	4.4495	3.9340	6.7147	6.6221
b(Å)	6.508	4.4290	4.2596	4.2806	6.2321	6.4688	6.6526

Table S2 Birefringence of calculation and experiment of α-BiB_3O_6 (about 1064nm)

	n_1	n_2	n_3	Δn
Experiment	1.7585	1.7854	1.9190	0.1605
calculation	1.8648	1.8789	2.013	0.1482

Table S3 Range of bond length and bong angle of BO_3, density of BO_3 in the unit cell, and distance of B atom out of O plane of BO_3, and dihedral angle of neighbouring BO_3

	Bond length (Å)	Bond angle (°)	Density	Dihedral angle(°)	Distance (Å)
$B2O_3$ (α-BiB_3O_6)	1.339-1.411	110.443-128.057	0.01796	89.335	0.044
$B1O_3$ (δ-BiB_3O_6)	1.376-1.392	116.793-125.29	0.00966	79.891	0.018
$B2O_3$ (ε-BiB_3O_6)	1.322-1.478	107.458-140.942	0.02244	47.593	0.011
$B3O_3$ (ε-BiB_3O_6)	1.340-1.424	110.107-134.198	0.02244	47.593	0.02

Table S4 Calculated value of SHG coefficients of α-BiB_3O_6 crystal as well as the contribution of each group (unit: pm/V)

	d_{16}	d_{14}	d_{22}	d_{23}
Calculated value	-4.37	-1.59	-4.89	-1.53
Only Bi-O polyhedra	-3.15	-1.87	-3.99	-0.85
Only BO_3	-0.49	0.40	-0.54	0.09
Only BO_4	-0.2	0.34	0.13	0.33
Only Bi	-0.5	-0.67	-0.97	-0.57

Table S5 Calculated value of SHG coefficients of δ-BiB_3O_6 crystal as well as the contribution of each group (unit: pm/V)

	d_{15}	d_{24}	d_{33}
Calculated value	-1.16	-0.36	4.53
Only Bi-O polyhedra	-0.22	0.06	3.43
Only BO_4	-0.86	-0.56	1.25
Only Bi	-0.22	-0.24	0.43