Supporting information

Chemical engineering of mixed halide hexaborates as nonlinear optical materials

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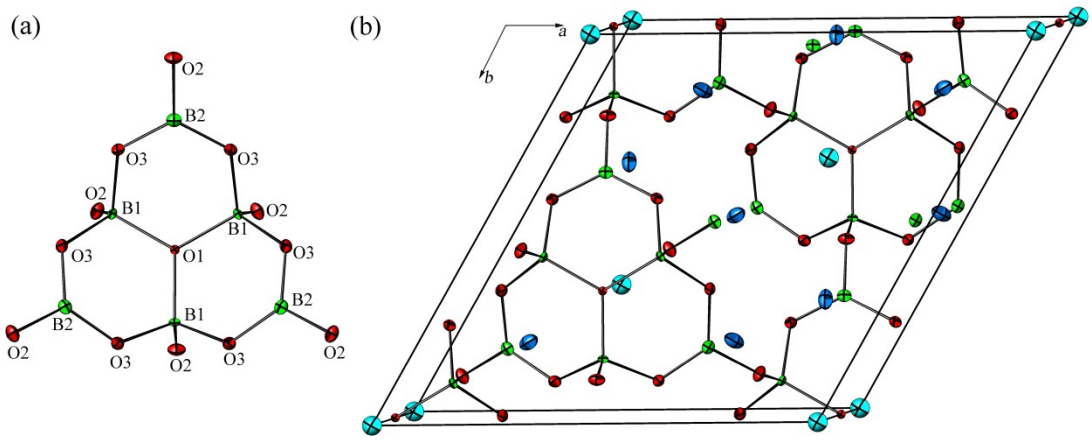

Figure S1. (a) The B_6O_{13} group and (b) crystal structure of $K_3B_6O_{10}Br_{0.53}Cl_{0.47}$ viewed along *c* direction. The displacement ellipsoids are drawn at the 50% probability level. (blue, K; cyan, Br/Cl; green, B; red, O).

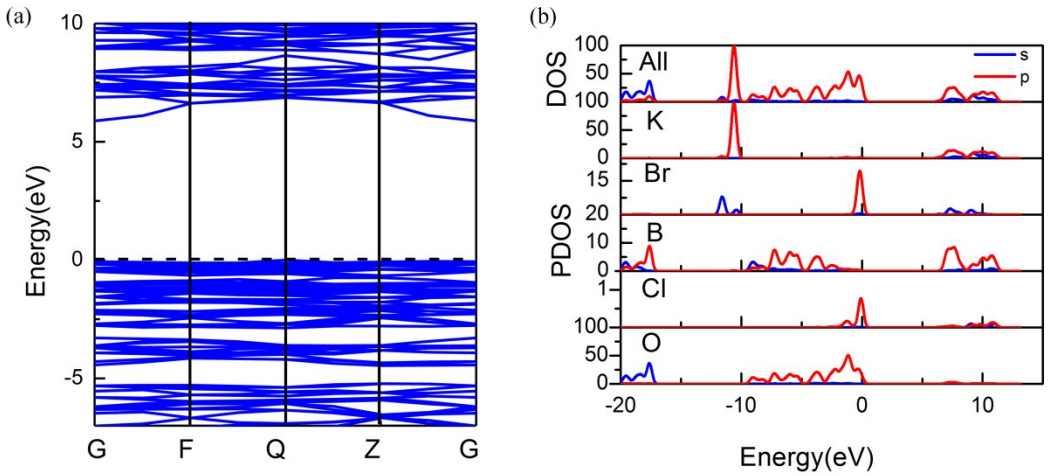

Figure S2. (a) Electronic band structure and (b) density of state (DOS) and partial density of state (PDOS) of $K_3B_6O_{10}Br_{0.53}Cl_{0.47}$.

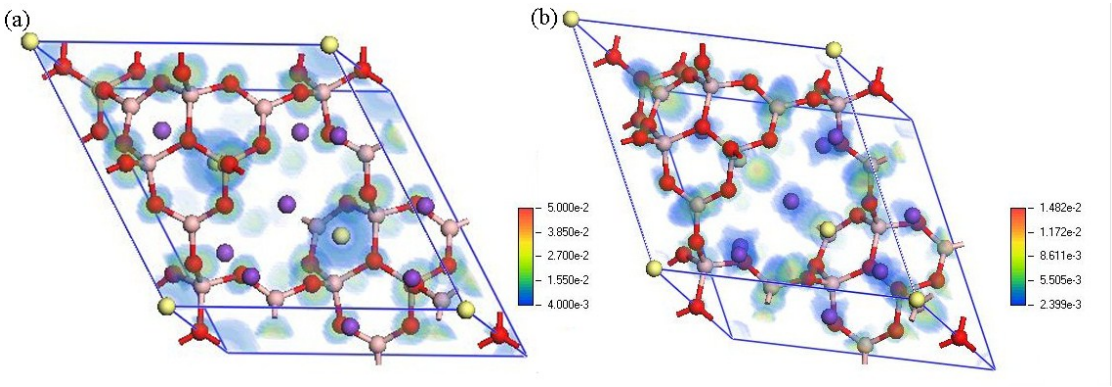

Figure S3. (a) Virtual-electron occupied and (b) unoccupied SHG density of $K_3B_6O_{10}Br$.

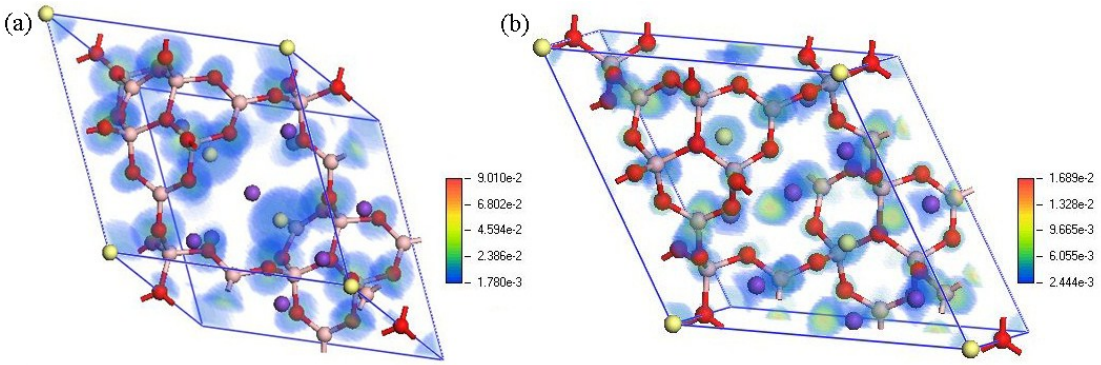

Figure S4. (a) Virtual-electron occupied and (b) unoccupied SHG density of $K_3B_6O_{10}Cl$.

Table S1. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $K_3B_6O_{10}Br_{0.79}Cl_{0.21}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	S.O.F	U_{eq}
Br1	0	0	0.00517(6)	0.792(7)	0.0218(2)
Cl1	0	0	0.00517(6)	0.208(7)	0.0218(2)
K1	0.81995(4)	0.63990(7)	0.11866(7)	1	0.0168(2)
O1	0	0	0.4506(4)	1	0.0054(7)
O2	0.55530(10)	0.44470(10)	-0.0539(2)	1	0.0113(4)
O3	0.76660(15)	0.76608(15)	0.37773(16)	1	0.0110(3)
B1	0.91278(16)	0.8256(3)	0.4564(3)	1	0.0064(5)
B2	0.6996(3)	0.84981(15)	0.3411(4)	1	0.0085(6)

Table S2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $K_3B_6O_{10}Br_{0.65}Cl_{0.35}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	S.O.F	U_{eq}
Br1	0	0	0.99481(8)	0.651(5)	0.0222(3)
Cl1	0	0	0.99481(8)	0.349(5)	0.0222(3)
K1	0.17982(4)	0.35964(8)	0.88081(7)	1	0.0170(3)
O1	0	0	0.5491(5)	1	0.0051(8)
O2	0.44468(11)	0.55532(11)	1.0538(2)	1	0.0104(5)
O3	0.23332(17)	0.23384(16)	0.62221(18)	1	0.0103(4)
B1	0.08719(18)	0.1744(4)	0.5429(3)	1	0.0061(6)
B2	0.3000(4)	0.15002(18)	0.6581(4)	1	0.0080(7)

Table S3. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $K_3B_6O_{10}Br_{0.53}Cl_{0.47}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	S.O.F	U_{eq}
Br1	0	0	0.99566(6)	0.527(3)	0.02295(17)
Cl1	0	0	0.99566(6)	0.473(3)	0.02295(17)
K1	0.17967(3)	0.35934(5)	0.88049(4)	1	0.01770(14)
O1	0	0	0.5491(3)	1	0.0051(5)
O2	0.44461(7)	0.55539(7)	0.05319(15)	1	0.0112(3)
O3	0.23345(10)	0.23407(10)	0.62179(12)	1	0.0111(2)
B1	0.08727(11)	0.1745(2)	0.5428(2)	1	0.0067(4)
B2	0.3006(2)	0.15029(11)	0.6577(3)	1	0.0088(4)

Table S4. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $K_3B_6O_{10}Br_{0.43}Cl_{0.57}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	S.O.F	U_{eq}
Br1	0	0	0.00377(8)	0.430(3)	0.0235(2)
Cl1	0	0	0.00377(8)	0.570(3)	0.0235(2)
K1	0.82048(3)	0.64097(6)	0.11967(5)	1	0.01824(16)
O1	0	0	0.4513(3)	1	0.0059(6)
O2	0.55545(8)	0.44455(8)	-0.05319(17)	1	0.0112(3)
O3	0.76664(11)	0.76582(11)	0.37843(13)	1	0.0115(2)
B1	0.91276(12)	0.8255(2)	0.4576(3)	1	0.0069(4)
B2	0.7002(3)	0.85008(13)	0.3429(3)	1	0.0089(5)

Table S5. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for $K_3B_6O_{10}Br_{0.25}Cl_{0.75}$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	S.O.F	U_{eq}
Br1	0	0	0.00190(9)	0.254(3)	0.0252(2)
Cl1	0	0	0.00190(9)	0.746(3)	0.0252(2)
K1	0.82068(3)	0.64137(5)	0.11970(4)	1	0.01845(13)
O1	0	0	0.4503(3)	1	0.0053(5)
O2	0.55572(7)	0.44428(7)	-0.05279(15)	1	0.0112(3)
O3	0.76640(10)	0.76569(9)	0.37862(11)	1	0.0110(2)
B1	0.91262(11)	0.8252(2)	0.4576(2)	1	0.0068(4)
B2	0.6998(2)	0.84988(11)	0.3419(2)	1	0.0088(4)

Table S6. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for $K_3B_6O_{10}Cl$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	S.O.F	U_{eq}
Cl1	0	0	0.00384(16)	1	0.0281(3)
K1	0.17902(3)	0.35804(7)	0.88208(3)	1	0.0196(2)
O1	0	0	0.5519(3)	1	0.0058(6)
O2	0.44433(8)	0.55567(8)	0.05487(19)	1	0.0121(4)
O3	0.23350(13)	0.23429(12)	0.62309(16)	1	0.0121(3)
B1	0.08740(13)	0.1748(3)	0.5444(3)	1	0.0081(5)
B2	0.3004(3)	0.15020(16)	0.6590(3)	1	0.0089(6)

Table S7. The important bond lengths (Å) for $K_3B_6O_{10}Br_{0.79}Cl_{0.21}$.

K1-O3	2.7808(13)	B1-O2	1.448(3)
K1-O3	2.7809(13)	B1-O3	1.463(2)
K1-O3	2.8047(15)	B1-O3	1.463(2)
K1-O3	2.8047(15)	B1-O1	1.527(3)
K1-O2	2.8464(12)	B2-O3	1.361(2)
K1-O2	2.8464(12)	B2-O3	1.361(2)
K1-X1	3.3077(7)	B2-O2	1.370(3)
K1-X1	3.3147(8)		

Table S8. The important bond lengths (Å) for $K_3B_6O_{10}Br_{0.65}Cl_{0.35}$.

K1-O3	2.7807(15)	B1-O2	1.443(4)
K1-O3	2.7808(15)	B1-O3	1.465(2)
K1-O3	2.8000(16)	B1-O3	1.465(2)
K1-O3	2.8000(16)	B1-O1	1.526(3)
K1-O2	2.8500(13)	B2-O3	1.357(2)
K1-O2	2.8500(13)	B2-O3	1.357(2)
K1-X1	3.3035(8)	B2-O2	1.375(4)
K1-X1	3.3144(9)		

Table S9. The important bond lengths (Å) for $K_3B_6O_{10}Br_{0.53}Cl_{0.47}$.

K1-O3	2.7773(9)	B1-O2	1.447(2)
K1-O3	2.7773(9)	B1-O3	1.4632(14)
K1-O3	2.7987(11)	B1-O3	1.4632(14)
K1-O3	2.7987(10)	B1-O1	1.527(2)
K1-O2	2.8489(8)	B2-O3	1.3596(14)
K1-O2	2.8489(8)	B2-O3	1.3596(14)
K1-X1	3.3027(5)	B2-O2	1.370(2)
K1-X1	3.3095(6)		

Table S10. The important bond lengths (Å) for $K_3B_6O_{10}Br_{0.43}Cl_{0.57}$.

K1-O3	2.7761(10)	B1-O2	1.442(3)
K1-O3	2.7762(10)	B1-O3	1.463(2)
K1-O3	2.7964(12)	B1-O3	1.463(2)
K1-O3	2.7964(12)	B1-O1	1.526(2)
K1-O2	2.8503(10)	B2-O3	1.357(2)
K1-O2	2.8503(10)	B2-O3	1.357(2)
K1-X1	3.3012(6)	B2-O2	1.379(3)
K1-X1	3.3070(7)		

Table S11. The important bond lengths (Å) for $K_3B_6O_{10}Br_{0.25}Cl_{0.75}$.

K1-O3	2.7723(9)	B1-O2	1.445(2)
K1-O3	2.7724(9)	B1-O3	1.463(2)
K1-O3	2.7969(10)	B1-O3	1.463(2)
K1-O3	2.7969(10)	B1-O1	1.528(2)
K1-O2	2.8490(8)	B2-O3	1.3598(13)
K1-O2	2.8490(8)	B2-O3	1.3598(13)
K1-X1	3.2994(6)	B2-O2	1.375(2)
K1-X1	3.3018(5)		

Table S12. The important bond lengths (Å) for $K_3B_6O_{10}Cl$.

K1-O3	2.7697(11)	B1-O2	1.444(3)
K1-O3	2.7697(11)	B1-O3	1.460(2)
K1-O3	2.7948(14)	B1-O3	1.460(2)
K1-O3	2.7948(14)	B1-O1	1.527(2)
K1-O2	2.8518(11)	B2-O3	1.358(2)
K1-O2	2.8518(11)	B2-O3	1.358(2)
K1-X1	3.2815(10)	B2-O2	1.376(4)
K1-X1	3.3051(8)		