Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Discovery of Excellent Ultraviolet Nonlinear Optical Materials in Chlorates and Bromates with Highly Stereochemically Active Lone Pairs

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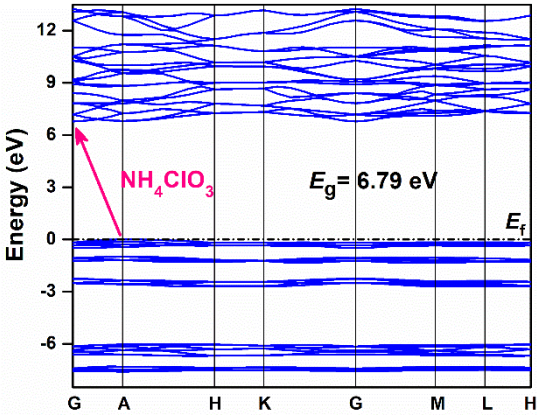
Figure S1. Calculated band structures for the halates by hybrid HSE06.



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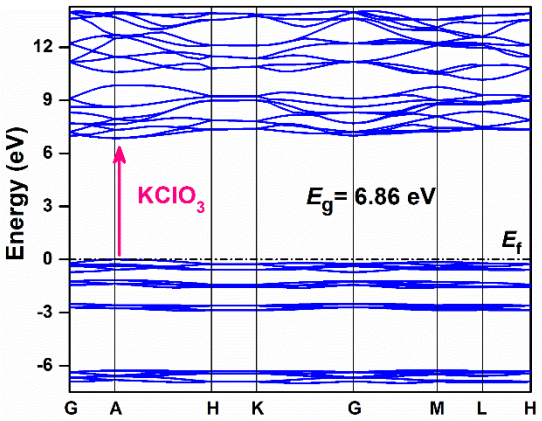

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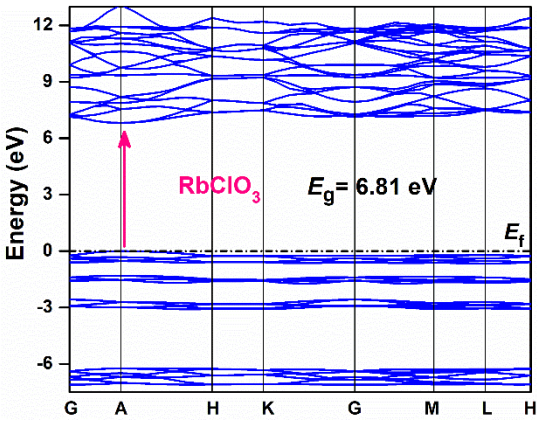

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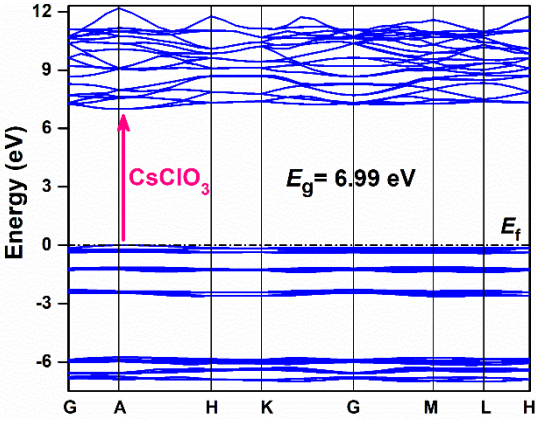
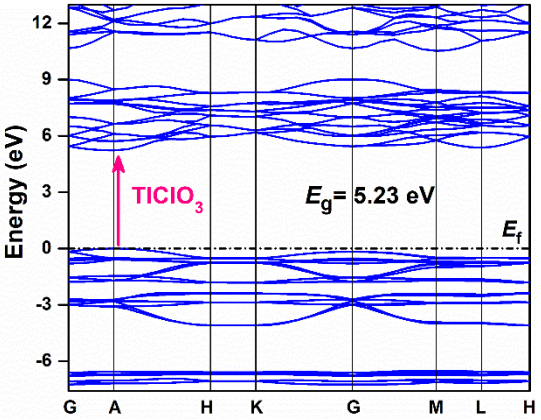
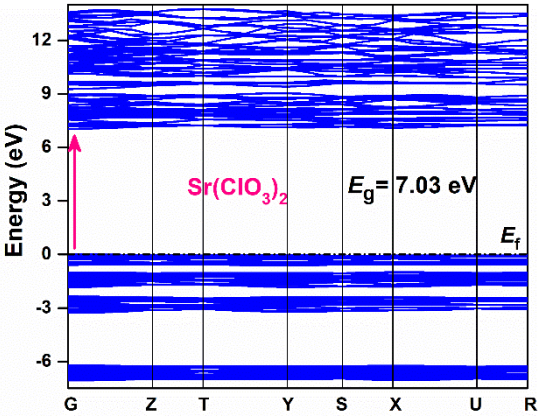

12
9
6
3
0
-3
-6
Energy (eV)
CsClO3
Eg= 6.99 eV
Ef
G A H K G M L H

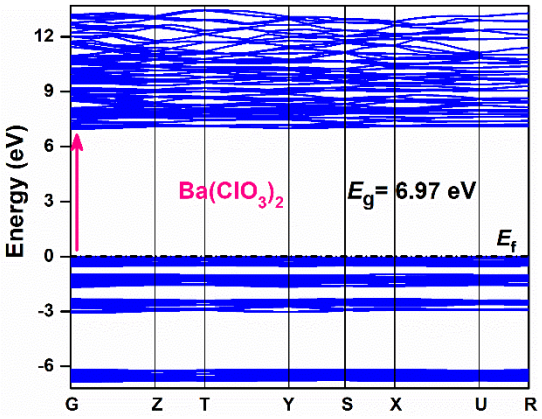
(d)


12
9
6
3
0
-3
-6
Energy (eV)
TlClO3
Eg= 5.23 eV
Ef
G A H K G M L H

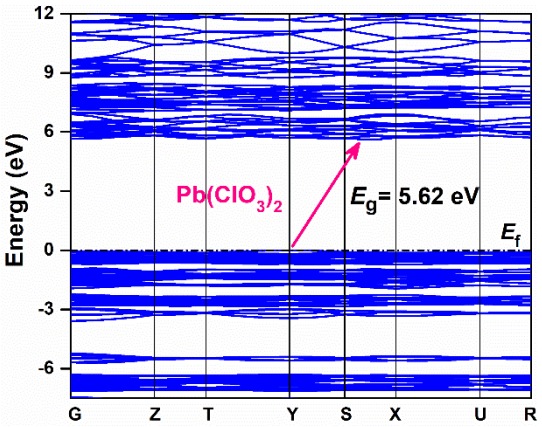
(e)


12
9
6
3
0
-3
-6
Energy (eV)
Sr(ClO3)2
Eg= 7.03 eV
Ef
G Z T Y S X U R

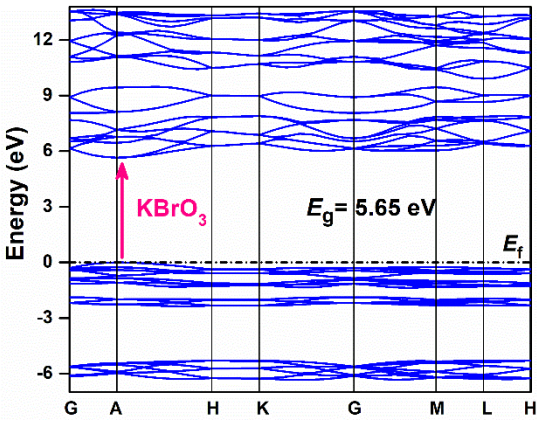
(f)


Energy (eV)
12
9
6
3
0
-3
-6
G
Z
T
Y
S
X
U
R
Ba(ClO3)2
Eg= 6.97 eV
Ef

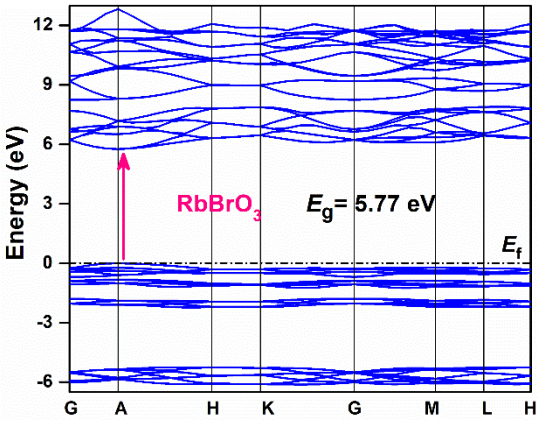
(g)


Energy (eV)
12
9
6
3
0
-3
-6
G
Z
T
Y
S
X
U
R
Pb(ClO3)2
Eg= 5.62 eV
Ef

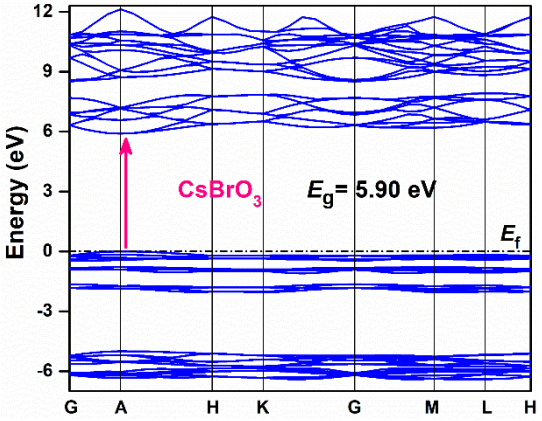
(h)


Energy (eV)
12
9
6
3
0
-3
-6
G
A
H
K
G
M
L
H
KBrO3
Eg= 5.65 eV
Ef

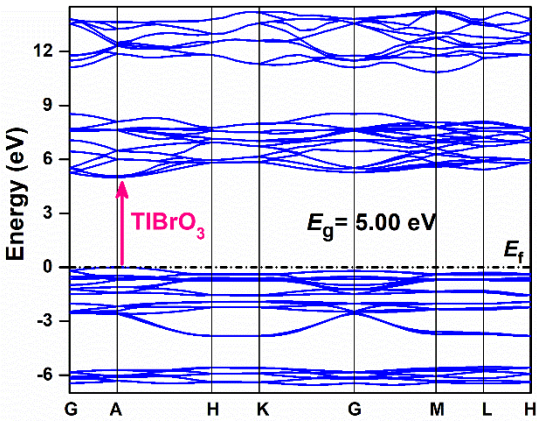
(i)


Energy (eV)
12
9
6
3
0
-3
-6
RbBrO3
Eg= 5.77 eV
Ef
G
A
H
K
G
M
L
H

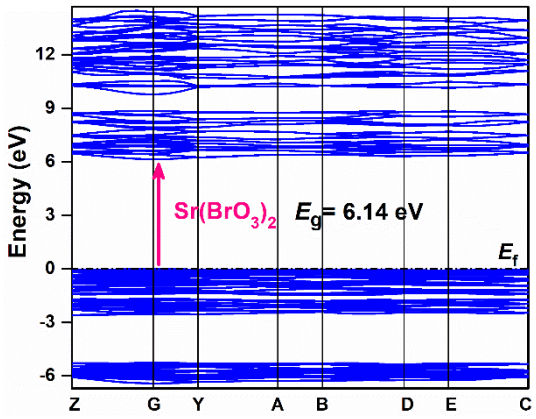
(j)


Energy (eV)
12
9
6
3
0
-3
-6
CsBrO3
Eg= 5.90 eV
Ef
G
A
H
K
G
M
L
H

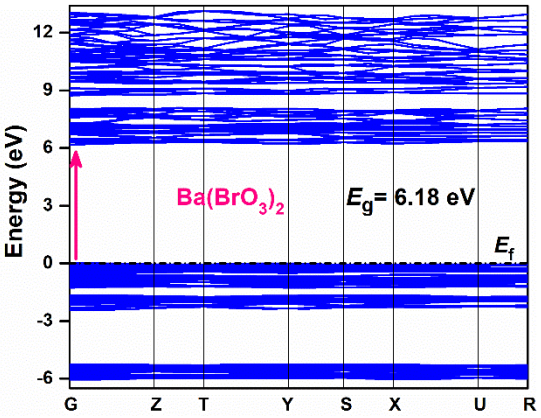
(k)


Energy (eV)
12
9
6
3
0
-3
-6
TlBrO3
Eg= 5.00 eV
Ef
G
A
H
K
G
M
L
H

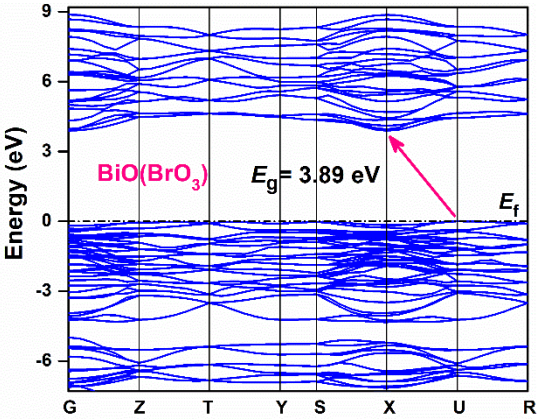
(l)


Energy (eV)
12
9
6
3
0
-3
-6
Z
G
Y
A
B
D
E
C
Sr(BrO3)2
Eg= 6.14 eV
Ef

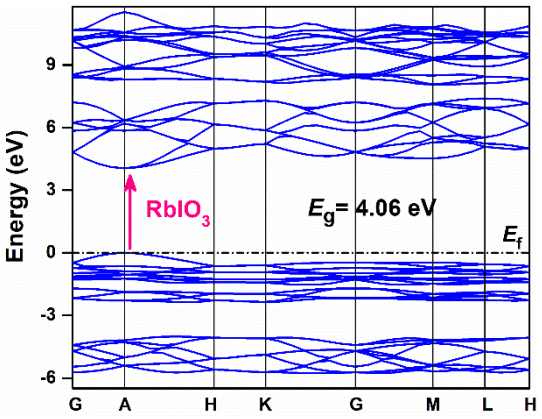
(m)


Energy (eV)
12
9
6
3
0
-3
-6
G
Z
T
Y
S
X
U
R
Ba(BrO3)2
Eg= 6.18 eV
Ef

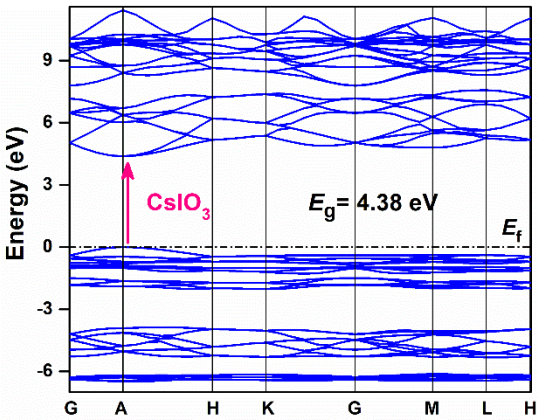
(n)


Energy (eV)
9
6
3
0
-3
-6
G
Z
T
Y
S
X
U
R
BiO(BrO3)
Eg= 3.89 eV
Ef

(o)

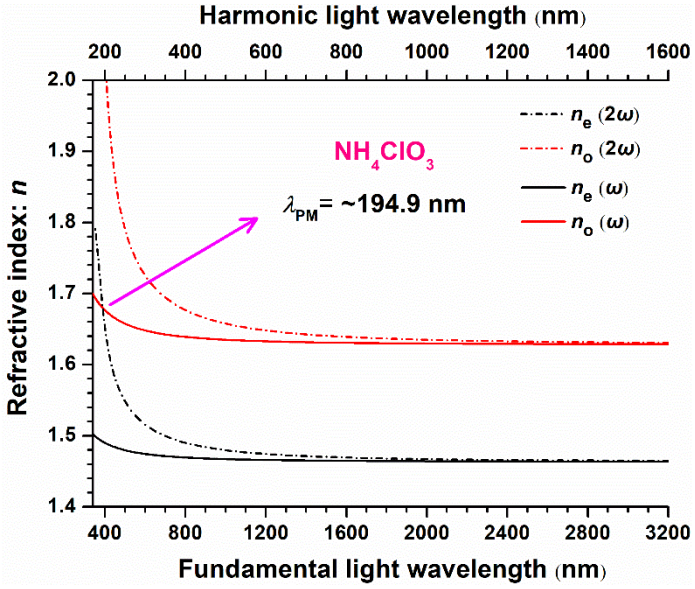

Energy (eV)
9
6
3
0
-3
-6
RbIO3
Eg= 4.06 eV
Ef
G
A
H
K
G
M
L
H

(p)

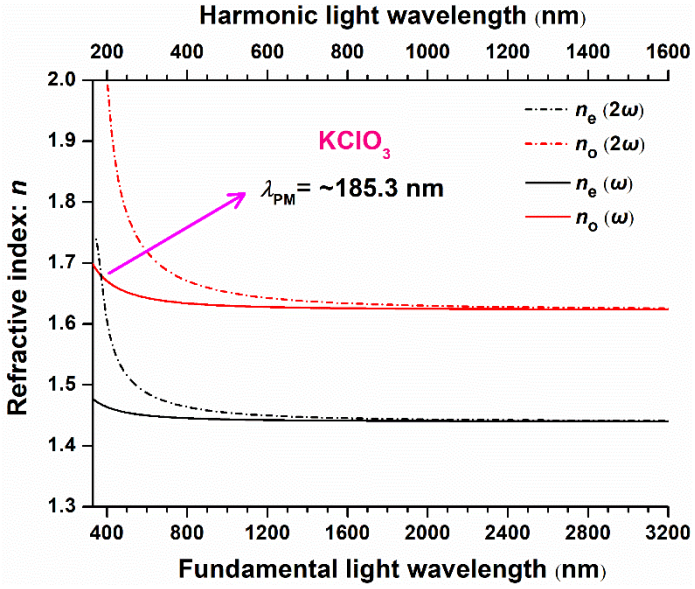

Energy (eV)
9
6
3
0
-3
-6
CsIO3
Eg= 4.38 eV
Ef
G
A
H
K
G
M
L
H

(q)

Figure S2. Calculated refractive index curves and the shortest PM wavelengths in the SHG process for the halates.



(a)



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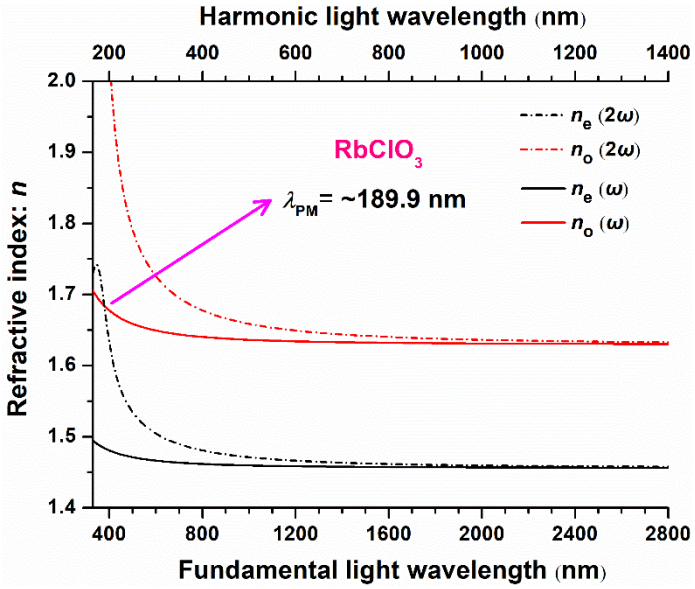
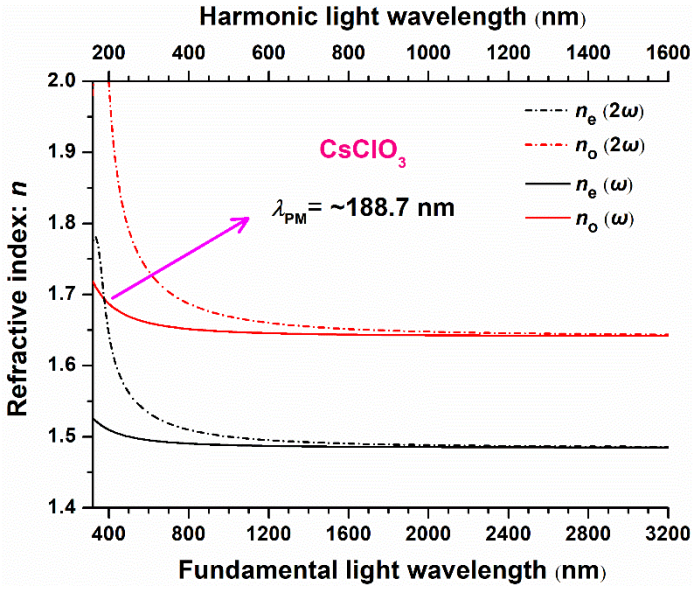
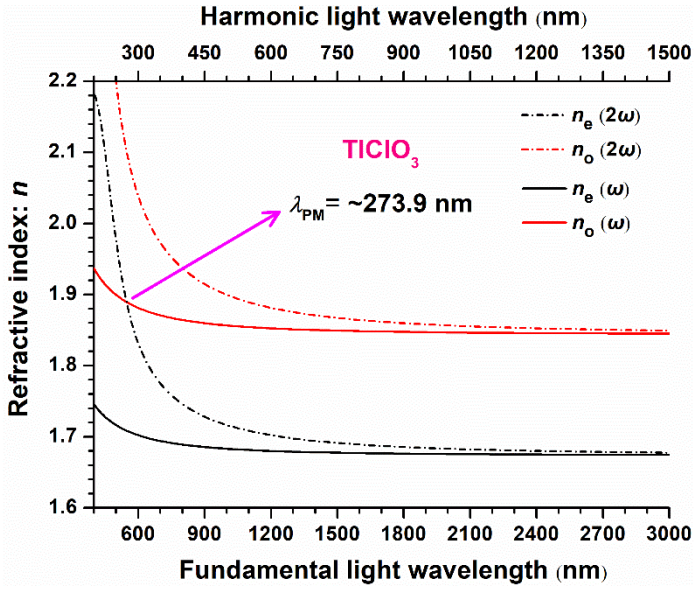

Harmonic light wavelength (nm)
200
400
600
800
1000
1200
1400
2.0
1.9
1.8
1.7
1.6
1.5
1.4
Refractive index: n
RbClO3
λPM= ~189.9 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
400
800
1200
1600
2000
2400
2800
Fundamental light wavelength (nm)

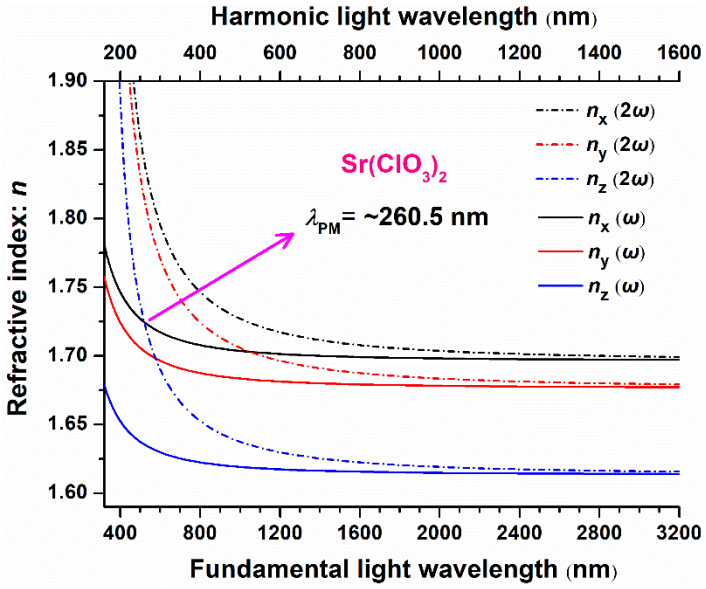
(c)


Harmonic light wavelength (nm)
200
400
600
800
1000
1200
1400
1600
2.0
1.9
1.8
1.7
1.6
1.5
1.4
Refractive index: n
CsClO3
λPM= ~188.7 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
400
800
1200
1600
2000
2400
2800
3200
Fundamental light wavelength (nm)

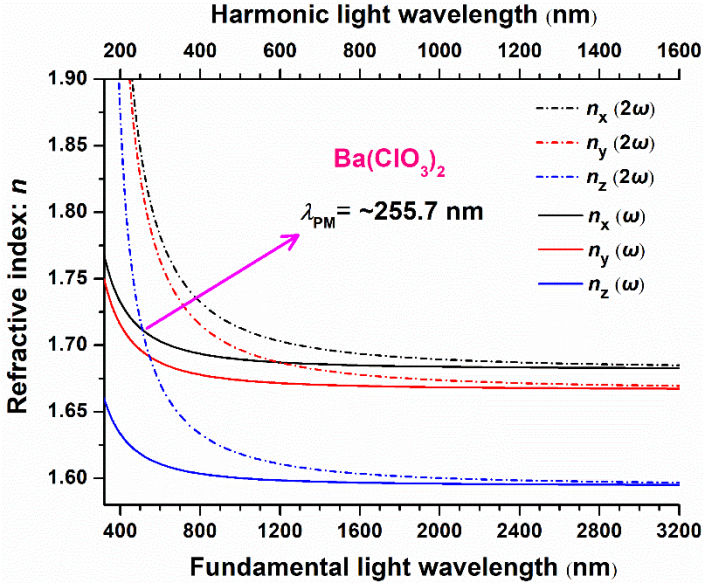
(d)


Harmonic light wavelength (nm)
300 450 600 750 900 1050 1200 1350 1500
2.2 2.1 2.0 1.9 1.8 1.7 1.6
Refractive index: n
TlClO3
λPM= ~273.9 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
600 900 1200 1500 1800 2100 2400 2700 3000
Fundamental light wavelength (nm)

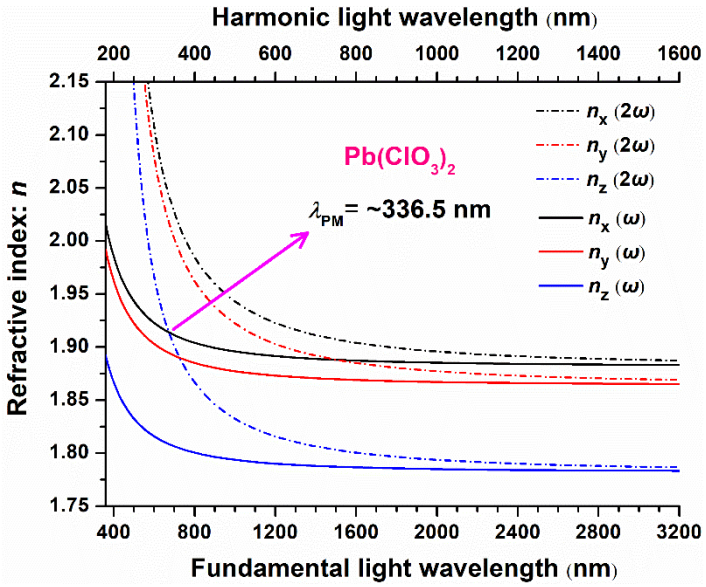
(e)


Harmonic light wavelength (nm)
200 400 600 800 1000 1200 1400 1600
1.90 1.85 1.80 1.75 1.70 1.65 1.60
Refractive index: n
Sr(ClO3)2
λPM= ~260.5 nm
nx (2ω)
ny (2ω)
nz (2ω)
nx (ω)
ny (ω)
nz (ω)
400 800 1200 1600 2000 2400 2800 3200
Fundamental light wavelength (nm)

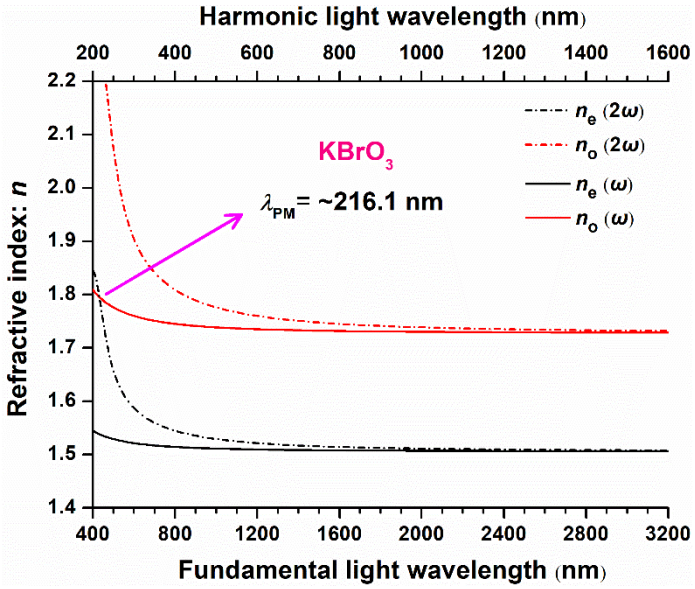
(f)


Harmonic light wavelength (nm)
200 400 600 800 1000 1200 1400 1600
1.90 1.85 1.80 1.75 1.70 1.65 1.60
Refractive index: n
Ba(ClO3)2
λPM= ~255.7 nm
nx (2ω)
ny (2ω)
nz (2ω)
nx (ω)
ny (ω)
nz (ω)
400 800 1200 1600 2000 2400 2800 3200
Fundamental light wavelength (nm)

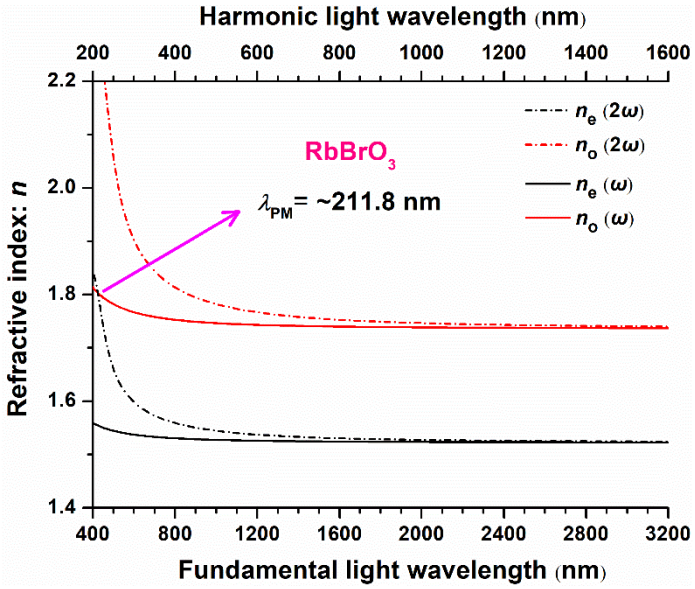
(g)


Harmonic light wavelength (nm)
200 400 600 800 1000 1200 1400 1600
2.15 2.10 2.05 2.00 1.95 1.90 1.85 1.80 1.75
Refractive index: n
Pb(ClO3)2
λPM= ~336.5 nm
nx (2ω)
ny (2ω)
nz (2ω)
nx (ω)
ny (ω)
nz (ω)
400 800 1200 1600 2000 2400 2800 3200
Fundamental light wavelength (nm)

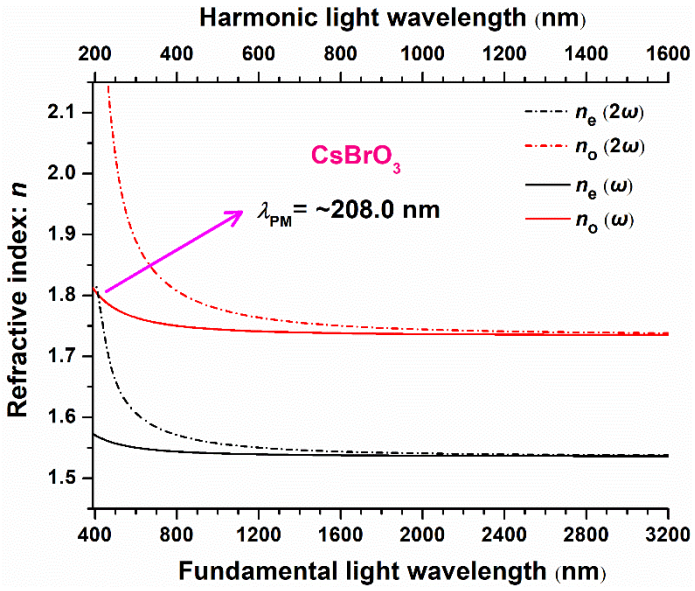
(h)


Harmonic light wavelength (nm)
200
400
600
800
1000
1200
1400
1600
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
Refractive index: n
KBrO3
λPM= ~216.1 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
400
800
1200
1600
2000
2400
2800
3200
Fundamental light wavelength (nm)

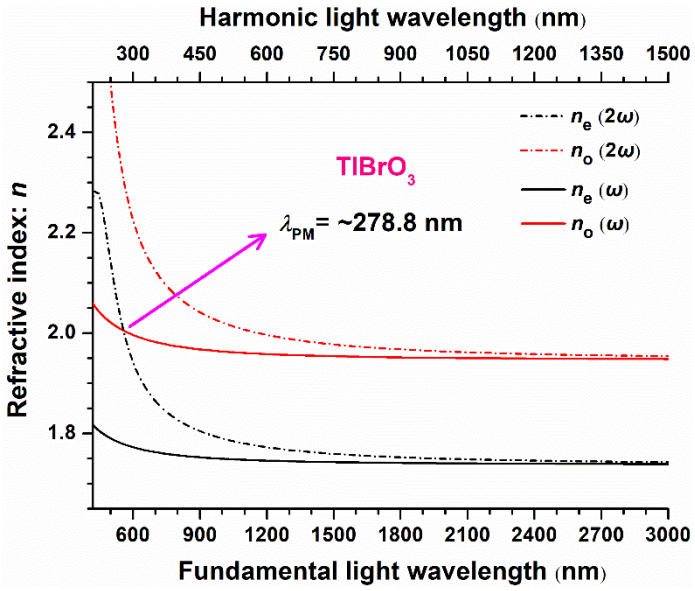
(i)


Harmonic light wavelength (nm)
200
400
600
800
1000
1200
1400
1600
2.2
2.0
1.8
1.6
1.4
Refractive index: n
RbBrO3
λPM= ~211.8 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
400
800
1200
1600
2000
2400
2800
3200
Fundamental light wavelength (nm)

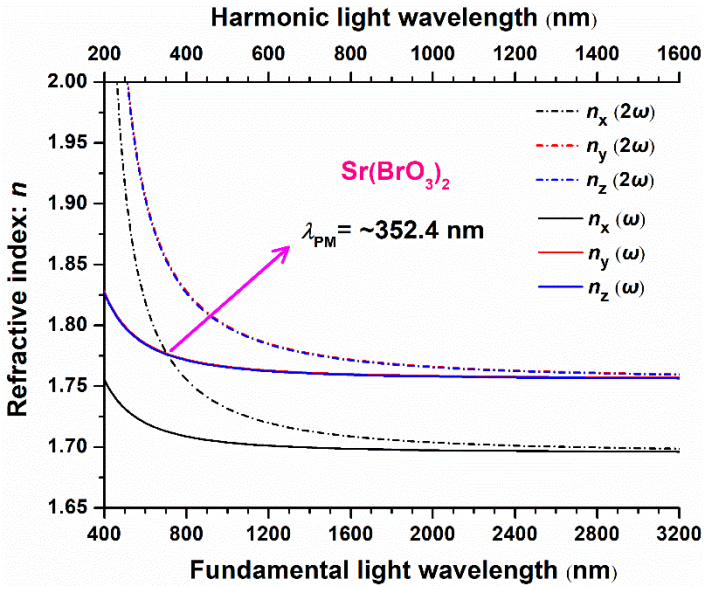
(j)


Harmonic light wavelength (nm)
200 400 600 800 1000 1200 1400 1600
2.1 2.0 1.9 1.8 1.7 1.6 1.5
Refractive index: n
CsBrO3
λPM= ~208.0 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
400 800 1200 1600 2000 2400 2800 3200
Fundamental light wavelength (nm)

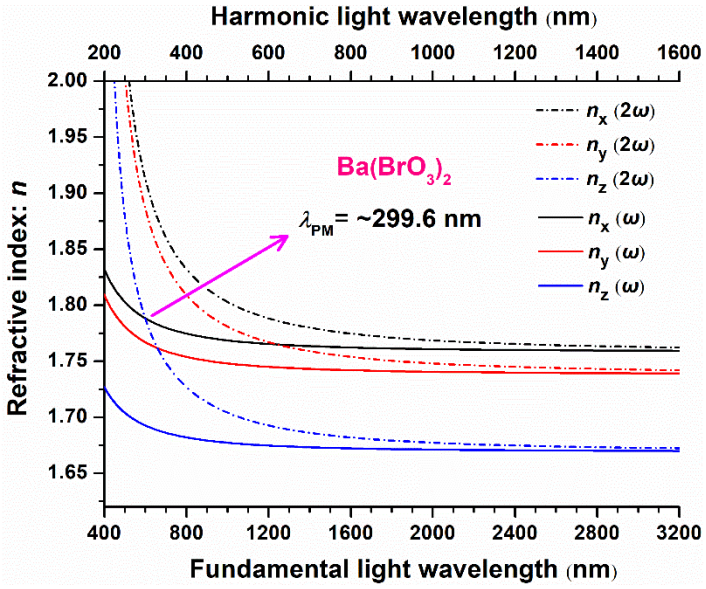
(k)


Harmonic light wavelength (nm)
300 450 600 750 900 1050 1200 1350 1500
2.4 2.2 2.0 1.8
Refractive index: n
TlBrO3
λPM= ~278.8 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
600 900 1200 1500 1800 2100 2400 2700 3000
Fundamental light wavelength (nm)

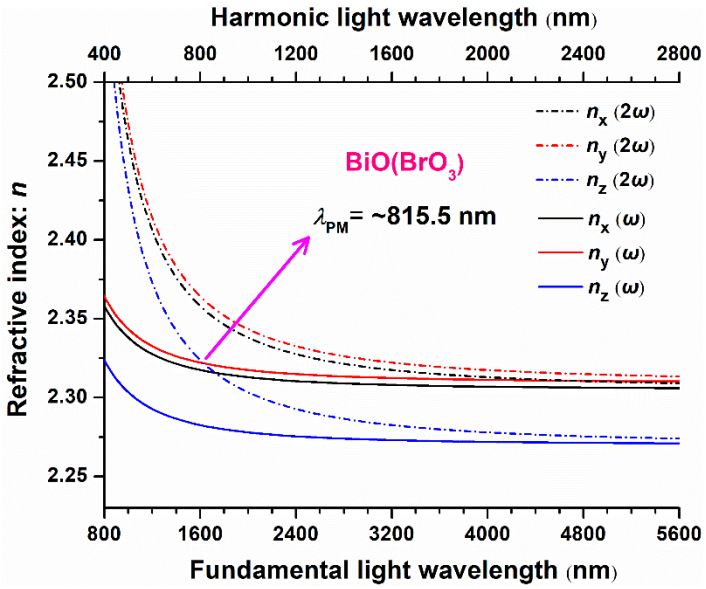
(l)


Harmonic light wavelength (nm)
200 400 600 800 1000 1200 1400 1600
2.00 1.95 1.90 1.85 1.80 1.75 1.70 1.65
Refractive index: n
400 800 1200 1600 2000 2400 2800 3200
Fundamental light wavelength (nm)
Sr(BrO3)2
λPM= ~352.4 nm
nx (2ω)
ny (2ω)
nz (2ω)
nx (ω)
ny (ω)
nz (ω)

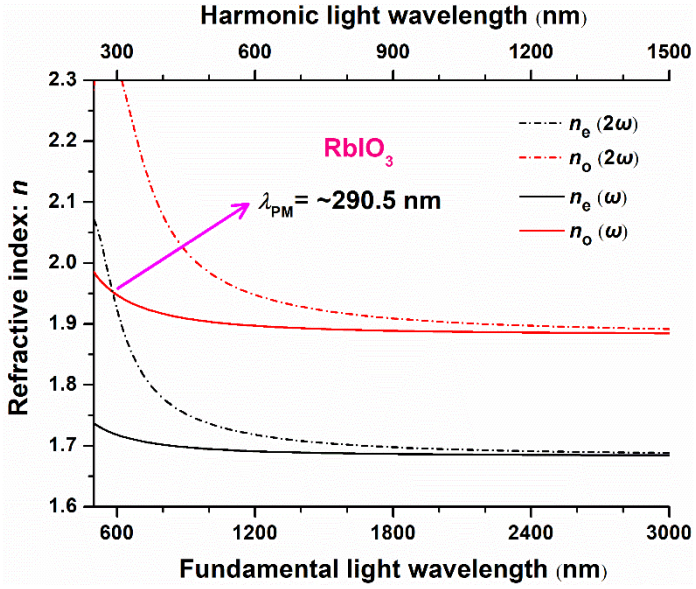
(m)


Harmonic light wavelength (nm)
200 400 600 800 1000 1200 1400 1600
2.00 1.95 1.90 1.85 1.80 1.75 1.70 1.65
Refractive index: n
400 800 1200 1600 2000 2400 2800 3200
Fundamental light wavelength (nm)
Ba(BrO3)2
λPM= ~299.6 nm
nx (2ω)
ny (2ω)
nz (2ω)
nx (ω)
ny (ω)
nz (ω)

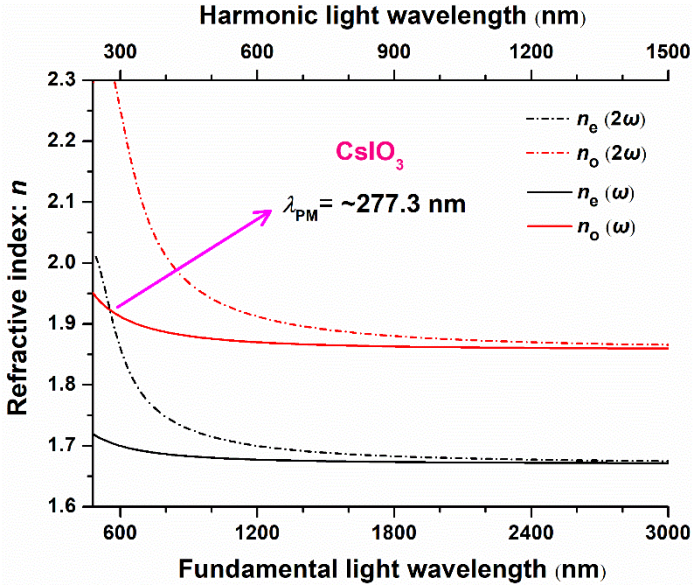
(n)


Harmonic light wavelength (nm)
400
800
1200
1600
2000
2400
2800
2.50
2.45
2.40
2.35
2.30
2.25
Refractive index: n
BiO(BrO3)
λPM= ~815.5 nm
nx (2ω)
ny (2ω)
nz (2ω)
nx (ω)
ny (ω)
nz (ω)
800
1600
2400
3200
4000
4800
5600
Fundamental light wavelength (nm)

(o)


Harmonic light wavelength (nm)
300
600
900
1200
1500
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
Refractive index: n
RbIO3
λPM= ~290.5 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
600
1200
1800
2400
3000
Fundamental light wavelength (nm)

(p)


Harmonic light wavelength (nm)
300
600
900
1200
1500
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
Refractive index: n
CsIO3
λPM= ~277.3 nm
ne (2ω)
no (2ω)
ne (ω)
no (ω)
600
1200
1800
2400
3000
Fundamental light wavelength (nm)

(q)

Figure S3. Visualization of the Pb^{2+}-$6s^2$, Tl^{+}-$6s^2$ and Cl^{5+}-$3s^2$ lone pairs (pink) through electron localization function (ELF) for $Pb(ClO_3)_2$ (a) and $TlClO_3$ (b) with η = 0.9.

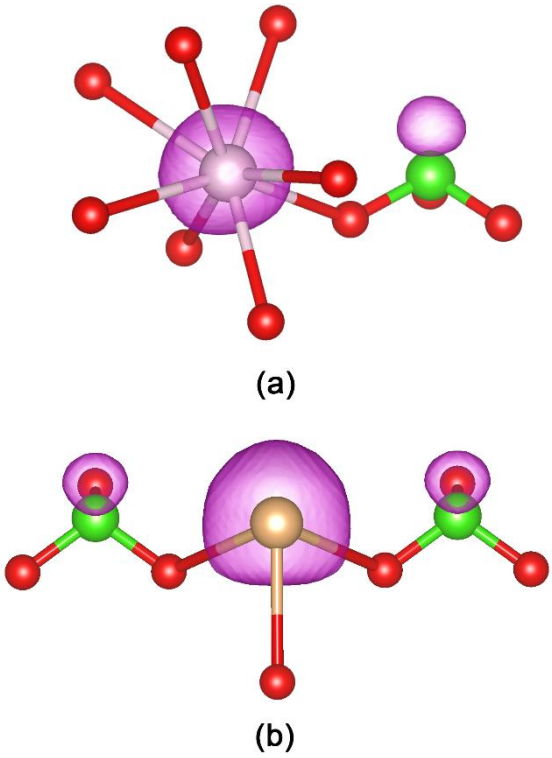
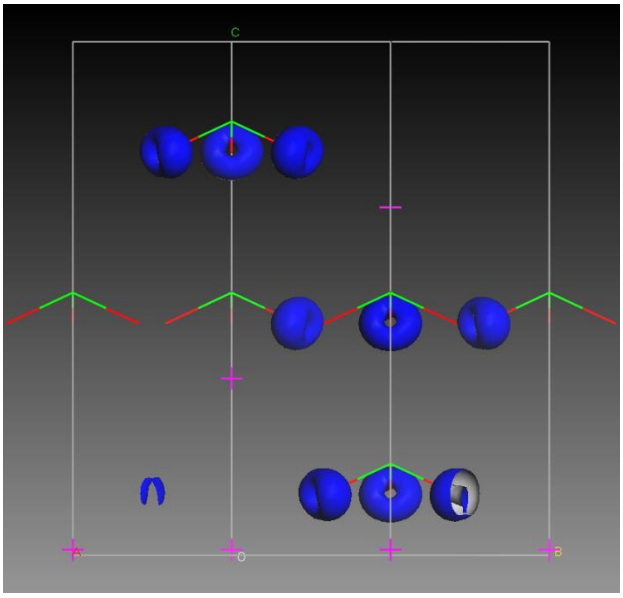
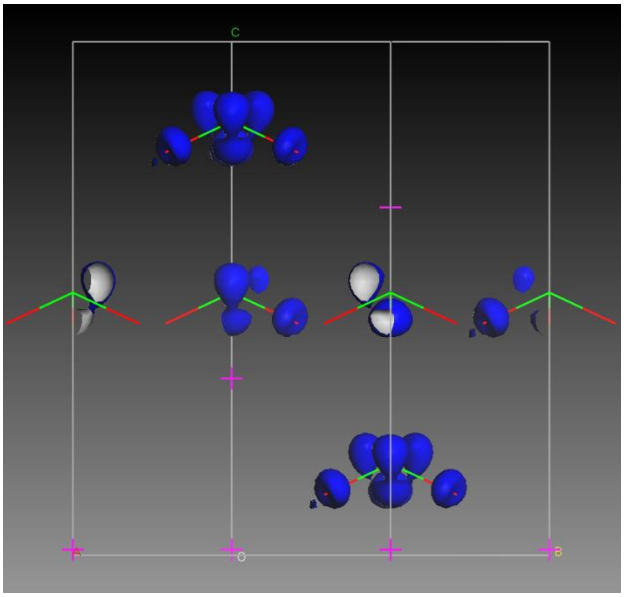


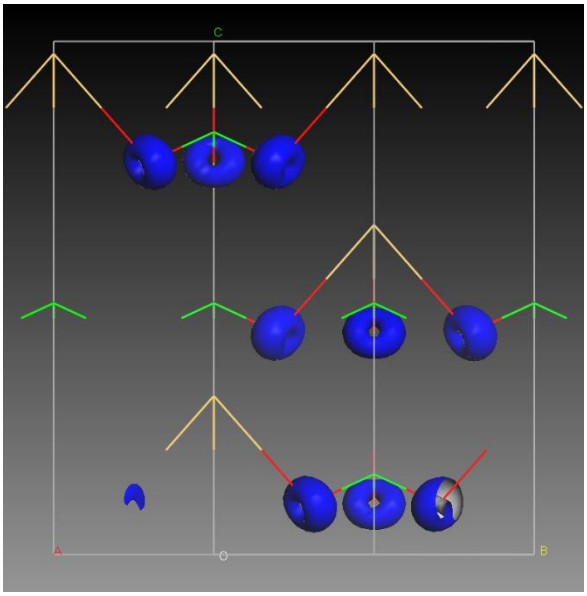
Figure S4. Polarizability anisotropy-weighted electron density (PAWED) plots for $KClO_3$ (a: VB; b: CB), $TlClO_3$ (c: VB; d: CB) and $Pb(ClO_3)_2$ (e: VB; f: CB).



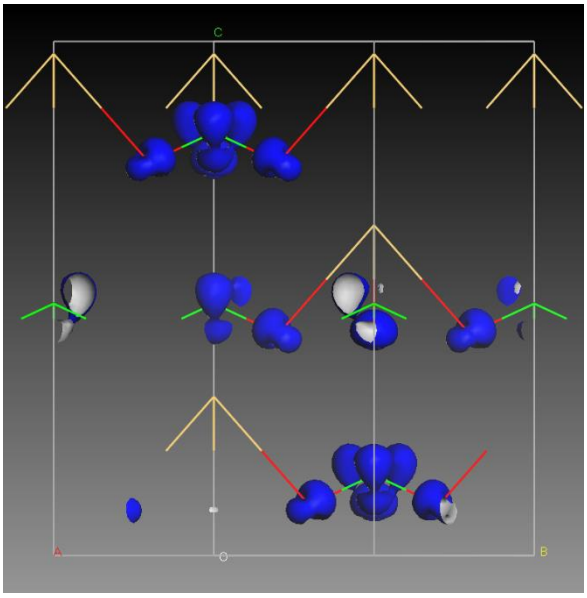
(a)



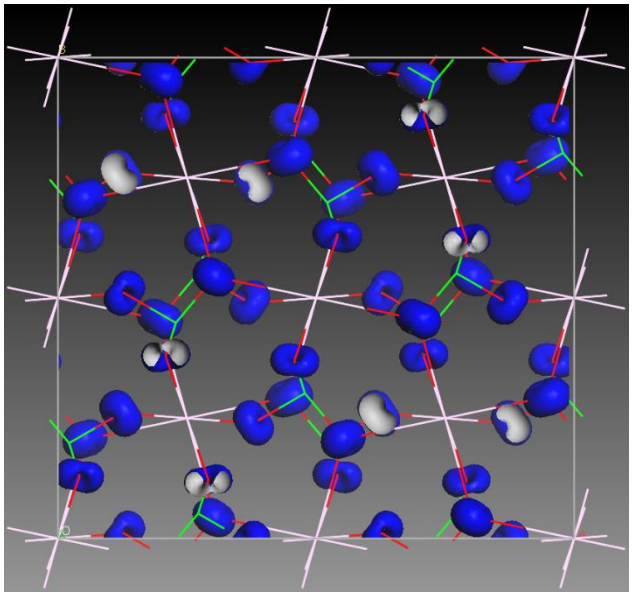
(b)



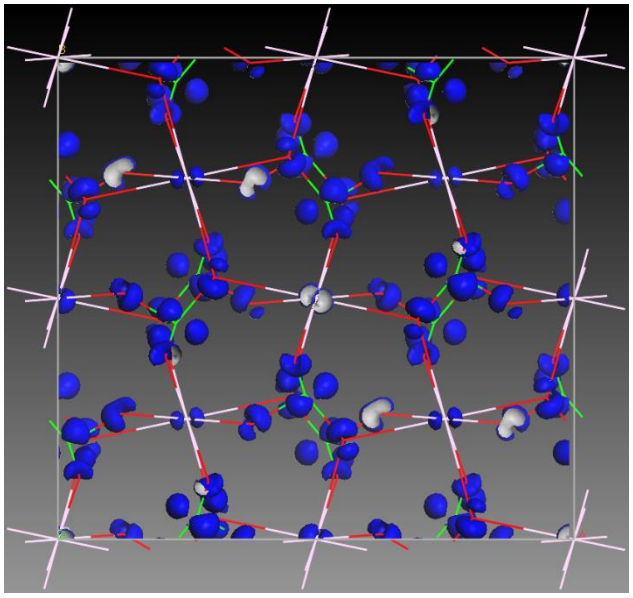
(c)



(d)



(e)



(f)