Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

$SrTi(IO_3)_6 \cdot 2H_2O$ and $SrSn(IO_3)_6$: Distinct Arrangements of Lone Pair Electrons Leading to Large Birefringences

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Table S1. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters (Å^2 × 10^3), and bond valence sum (BVS) for $SrTi(IO_3)_6{\cdot}2H_2O$, $(H_3O)_2Ti(IO_3)_6$, and $SrSn(IO_3)_6$, respectively. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atoms	x	y	z	U_{eq}	BVS
			$SrTi(IO_3)_6{\cdot}2H_2O$		
Sr(1)	0	0	10000	15(1)	2.23
Ti(1)	6667	3333	8333	10(1)	4.56
I(1)	3724(1)	522(1)	9615(1)	12(1)	5.02
O(1)	0	0	8059(6)	93(3)	0.42
O(2)	5194(3)	2177(3)	9255(3)	20(1)	2.29
O(3)	2702(3)	1249(3)	9982(3)	22(1)	1.99
O(4)	4364(3)	364(3)	10885(3)	22(1)	1.73
			$(H_3O)_2Ti(IO_3)_6$		
Ti(1)	10000	10000	0	22(1)	4.17
I(1)	6843(1)	7379(1)	1078(1)	16(1)	4.92
O(1)	3333	6667	249(9)	39(2)	/
O(2)	8406(4)	9094(4)	1016(3)	26(1)	2.17
O(3)	6008(4)	7876(4)	2144(3)	19(1)	1.68
O(4)	6124(5)	7587(4)	-273(3)	32(1)	1.75
			$SrSn(IO_3)_6$		
Sr(1)	0	0	5000	14(1)	1.93
Sn(1)	0	0	0	8(1)	3.95
I(1)	2265(1)	2664(1)	2158(1)	8(1)	4.89
O(1)	2091(3)	3853(3)	1137(3)	12(1)	1.96
O(2)	614(3)	1968(3)	3000(3)	14(1)	1.78
O(3)	1786(3)	1215(3)	1038(3)	11(1)	2.12

Table S2. Selected bond lengths (Å) and angles (deg.) for $SrTi(IO_3)_6 \cdot 2H_2O$, $(H_3O)_2Ti(IO_3)_6$, and $SrSn(IO_3)_6$, respectively.

$SrTi(IO_3)_6 \cdot 2H_2O$			
Sr(1)-O(1)	2.433(8)	Ti(1)-O(2)	1.915(3)
Sr(1)-O(1)#1	2.433(8)	Ti(1)-O(2)#8	1.915(3)
Sr(1)-O(3)#2	2.664(3)	Ti(1)-O(2)#9	1.915(3)
Sr(1)-O(3)#3	2.664(3)	Ti(1)-O(2)#10	1.915(3)
Sr(1)-O(3)#1	2.664(3)	I(1)-O(3)	1.790(3)
Sr(1)-O(3)#4	2.664(3)	I(1)-O(4)	1.797(3)
Sr(1)-O(3)#5	2.664(3)	I(1)-O(2)	1.843(3)
Sr(1)-O(3)	2.664(3)	O(1)-H(1)	0.8221
Ti(1)-O(2)#6	1.915(3)	O(1)-H(1)#5	0.82(13)
Ti(1)-O(2)#7	1.915(3)	O(1)-H(1)#3	0.82(13)
O(1)-Sr(1)-O(1)#1	180	O(3)#2-Sr(1)-O(3)	60.007(3)
O(1)-Sr(1)-O(3)#2	90.49(7)	O(3)#3-Sr(1)-O(3)	119.993(2)
O(1)#1-Sr(1)-O(3)#2	89.51(7)	O(3)#1-Sr(1)-O(3)	180
O(1)-Sr(1)-O(3)#3	89.51(7)	O(3)#4-Sr(1)-O(3)	60.007(3)
O(1)#1-Sr(1)-O(3)#3	90.49(7)	O(3)#5-Sr(1)-O(3)	119.993(3)
O(3)#2-Sr(1)-O(3)#3	180.00(14)	O(2)#6-Ti(1)-O(2)#7	180
O(1)-Sr(1)-O(3)#1	90.49(7)	O(2)#6-Ti(1)-O(2)	92.64(14)
O(1)#1-Sr(1)-O(3)#1	89.51(7)	O(2)#7-Ti(1)-O(2)	87.36(14)
O(3)#2-Sr(1)-O(3)#1	119.993(2)	O(2)#6-Ti(1)-O(2)#8	87.37(14)
O(3)#3-Sr(1)-O(3)#1	60.007(3)	O(2)#7-Ti(1)-O(2)#8	92.63(14)
O(1)-Sr(1)-O(3)#4	90.49(7)	O(2)-Ti(1)-O(2)#8	180.00(15)

O(1)#1-Sr(1)-O(3)#4	89.51(7)	O(2)#6-Ti(1)-O(2)#9	92.64(14)
O(3)#2-Sr(1)-O(3)#4	119.993(3)	O(2)#7-Ti(1)-O(2)#9	87.36(14)
O(3)#3-Sr(1)-O(3)#4	60.007(3)	O(2)-Ti(1)-O(2)#9	87.36(14)
O(3)#1-Sr(1)-O(3)#4	119.993(3)	O(2)#8-Ti(1)-O(2)#9	92.64(14)
O(1)-Sr(1)-O(3)#5	89.51(7)	O(2)#6-Ti(1)-O(2)#10	87.36(14)
O(1)#1-Sr(1)-O(3)#5	90.49(7)	O(2)#7-Ti(1)-O(2)#10	92.63(14)
O(3)#2-Sr(1)-O(3)#5	60.007(3)	O(2)-Ti(1)-O(2)#10	92.64(14)
O(3)#3-Sr(1)-O(3)#5	119.993(3)	O(2)#8-Ti(1)-O(2)#10	87.36(14)
O(3)#1-Sr(1)-O(3)#5	60.007(3)	O(2)#9-Ti(1)-O(2)#10	180
O(3)#4-Sr(1)-O(3)#5	180.00(14)	O(3)-I(1)-O(4)	101.98(15)
O(1)-Sr(1)-O(3)	89.51(7)	O(3)-I(1)-O(2)	93.30(13)
O(1)#1-Sr(1)-O(3)	90.49(7)	O(4)-I(1)-O(2)	96.48(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+2 #2 x-y,x,-z+2 #3 -x+y,-x,z #4 -y,x-y,z #5 y,-x+y,-z+2 #6 y+1/3,-x+y+2/3,-z+5/3

#7 -y+1,x-y,z #8 -x+y+1,-x+1,z #9 -x+4/3,-y+2/3,-z+5/3 #10 x-y+1/3,x-1/3,-z+5/3

$(H_3O)_2Ti(IO_3)_6$

Ti(1)-O(2)#1	1.946(5)	Ti(1)-O(2)	1.946(5)
Ti(1)-O(2)#2	1.946(5)	I(1)-O(3)	1.790(5)
Ti(1)-O(2)#3	1.946(5)	I(1)-O(4)	1.807(5)
Ti(1)-O(2)#4	1.946(5)	I(1)-O(2)	1.860(6)
Ti(1)-O(2)#5	1.946(5)		

O(2)#1-Ti(1)-O(2)#2	180	O(2)#4-Ti(1)-O(2)#5	91.6(2)
O(2)#1-Ti(1)-O(2)#3	88.4(2)	O(2)#1-Ti(1)-O(2)	91.6(2)

O(2)#2-Ti(1)-O(2)#3	91.6(2)	O(2)#2-Ti(1)-O(2)	88.4(2)
O(2)#1-Ti(1)-O(2)#4	91.6(2)	O(2)#3-Ti(1)-O(2)	91.6(2)
O(2)#2-Ti(1)-O(2)#4	88.4(2)	O(2)#4-Ti(1)-O(2)	88.4(2)
O(2)#3-Ti(1)-O(2)#4	180	O(2)#5-Ti(1)-O(2)	180.0(2)
O(2)#1-Ti(1)-O(2)#5	88.4(2)	O(3)-I(1)-O(4)	101.1(3)
O(2)#2-Ti(1)-O(2)#5	91.6(2)	O(3)-I(1)-O(2)	94.21(17)
O(2)#3-Ti(1)-O(2)#5	88.4(2)	O(4)-I(1)-O(2)	94.99(18)

Symmetry transformations used to generate equivalent atoms:

#1 y,-x+y+1,-z #2 -y+2,x-y+1,z #3 -x+2,-y+2,-z #4 x-y+1,x,-z #5 -x+y+1,-x+2,z

$SrSn(IO_3)_6$

Sr(1)-O(1)#1	2.704(3)	Sr(1)-O(2)#11	2.912(3)
Sr(1)-O(1)#2	2.704(3)	Sn(1)-O(3)	2.059(3)
Sr(1)-O(1)#3	2.704(3)	Sn(1)-O(3)#12	2.059(3)
Sr(1)-O(1)#4	2.704(3)	Sn(1)-O(3)#13	2.059(3)
Sr(1)-O(1)#5	2.704(3)	Sn(1)-O(3)#8	2.059(3)
Sr(1)-O(1)#6	2.704(3)	Sn(1)-O(3)#14	2.059(3)
Sr(1)-O(2)	2.912(3)	Sn(1)-O(3)#10	2.059(3)
Sr(1)-O(2)#7	2.912(3)	I(1)-O(1)	1.792(3)
Sr(1)-O(2)#8	2.912(3)	I(1)-O(2)	1.811(3)
Sr(1)-O(2)#9	2.912(3)	I(1)-O(3)	1.859(3)
Sr(1)-O(2)#10	2.912(3)		

O(1)#1-Sr(1)-O(1)#2	180	O(2)-Sr(1)-O(2)#9	111.81(10)
O(1)#1-Sr(1)-O(1)#3	115.42(4)	O(2)#7-Sr(1)-O(2)#9	68.19(10)
O(1)#2-Sr(1)-O(1)#3	64.58(4)	O(2)#8-Sr(1)-O(2)#9	111.81(10)

O(1)#1-Sr(1)-O(1)#4	64.58(4)	O(1)#1-Sr(1)-O(2)#10	113.47(9)
O(1)#2-Sr(1)-O(1)#4	115.42(4)	O(1)#2-Sr(1)-O(2)#10	66.53(9)
O(1)#3-Sr(1)-O(1)#4	180	O(1)#3-Sr(1)-O(2)#10	123.92(9)
O(1)#1-Sr(1)-O(1)#5	115.41(4)	O(1)#4-Sr(1)-O(2)#10	56.08(9)
O(1)#2-Sr(1)-O(1)#5	64.59(4)	O(1)#5-Sr(1)-O(2)#10	62.65(9)
O(1)#3-Sr(1)-O(1)#5	115.41(4)	O(1)#6-Sr(1)-O(2)#10	117.35(9)
O(1)#4-Sr(1)-O(1)#5	64.59(4)	O(2)-Sr(1)-O(2)#10	68.19(10)
O(1)#1-Sr(1)-O(1)#6	64.59(4)	O(2)#7-Sr(1)-O(2)#10	111.81(11)
O(1)#2-Sr(1)-O(1)#6	115.41(4)	O(2)#8-Sr(1)-O(2)#10	68.19(10)
O(1)#3-Sr(1)-O(1)#6	64.59(4)	O(2)#9-Sr(1)-O(2)#10	180
O(1)#4-Sr(1)-O(1)#6	115.41(4)	O(1)#1-Sr(1)-O(2)#11	117.35(9)
O(1)#5-Sr(1)-O(1)#6	180.00(12)	O(1)#2-Sr(1)-O(2)#11	62.65(9)
O(1)#1-Sr(1)-O(2)	62.65(9)	O(1)#3-Sr(1)-O(2)#11	66.53(9)
O(1)#2-Sr(1)-O(2)	117.35(9)	O(1)#4-Sr(1)-O(2)#11	113.47(9)
O(1)#3-Sr(1)-O(2)	113.47(9)	O(1)#5-Sr(1)-O(2)#11	56.08(9)
O(1)#4-Sr(1)-O(2)	66.53(9)	O(1)#6-Sr(1)-O(2)#11	123.92(9)
O(1)#5-Sr(1)-O(2)	123.92(9)	O(2)-Sr(1)-O(2)#11	180.00(14)
O(1)#6-Sr(1)-O(2)	56.08(9)	O(2)#7-Sr(1)-O(2)#11	68.19(11)
O(1)#1-Sr(1)-O(2)#7	56.08(9)	O(2)#8-Sr(1)-O(2)#11	111.81(11)
O(1)#2-Sr(1)-O(2)#7	123.92(9)	O(2)#9-Sr(1)-O(2)#11	68.19(10)
O(1)#3-Sr(1)-O(2)#7	117.35(9)	O(2)#10-Sr(1)-O(2)#11	111.81(10)
O(1)#4-Sr(1)-O(2)#7	62.65(9)	O(3)-Sn(1)-O(3)#12	180
O(1)#5-Sr(1)-O(2)#7	66.53(9)	O(3)-Sn(1)-O(3)#13	88.22(12)
O(1)#6-Sr(1)-O(2)#7	113.47(9)	O(3)#12-Sn(1)-O(3)#13	91.78(12)
O(2)-Sr(1)-O(2)#7	111.81(11)	O(3)-Sn(1)-O(3)#8	91.78(12)
O(1)#1-Sr(1)-O(2)#8	123.92(9)	O(3)#12-Sn(1)-O(3)#8	88.22(12)
O(1)#2-Sr(1)-O(2)#8	56.08(9)	O(3)#13-Sn(1)-O(3)#8	88.22(12)

O(1)#3-Sr(1)-O(2)#8	62.65(9)	O(3)-Sn(1)-O(3)#14	88.22(12)
O(1)#4-Sr(1)-O(2)#8	117.35(9)	O(3)#12-Sn(1)-O(3)#14	91.78(12)
O(1)#5-Sr(1)-O(2)#8	113.47(9)	O(3)#13-Sn(1)-O(3)#14	91.78(12)
O(1)#6-Sr(1)-O(2)#8	66.53(9)	O(3)#8-Sn(1)-O(3)#14	180.00(17)
O(2)-Sr(1)-O(2)#8	68.19(10)	O(3)-Sn(1)-O(3)#10	91.78(12)
O(2)#7-Sr(1)-O(2)#8	180	O(3)#12-Sn(1)-O(3)#10	88.22(12)
O(1)#1-Sr(1)-O(2)#9	66.53(9)	O(3)#13-Sn(1)-O(3)#10	180.0(2)
O(1)#2-Sr(1)-O(2)#9	113.47(9)	O(3)#8-Sn(1)-O(3)#10	91.78(12)
O(1)#3-Sr(1)-O(2)#9	56.08(9)	O(3)#14-Sn(1)-O(3)#10	88.22(12)
O(1)#4-Sr(1)-O(2)#9	123.92(9)	O(1)-I(1)-O(2)	100.91(15)
O(1)#5-Sr(1)-O(2)#9	117.35(9)	O(1)-I(1)-O(3)	95.52(14)
O(1)#6-Sr(1)-O(2)#9	62.65(9)	O(2)-I(1)-O(3)	101.18(14)

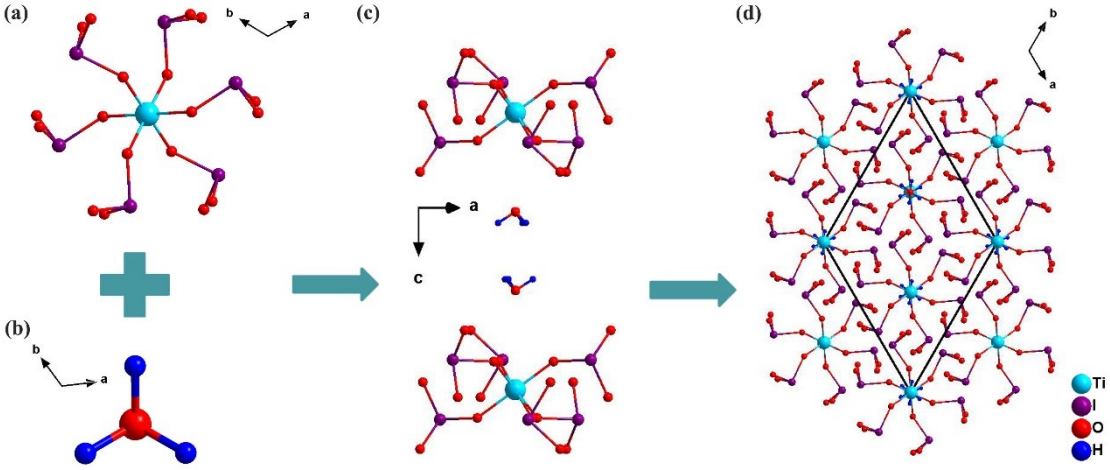
Symmetry transformations used to generate equivalent atoms:

#1 -x+1/3,-y+2/3,-z+2/3 #2 x-1/3,y-2/3,z+1/3 #3 y-2/3,-x+y-1/3,-z+2/3 #4 -y+2/3,x-y+1/3,z+1/3

#5 x-y+1/3,x-1/3,-z+2/3 #6 -x+y-1/3,-x+1/3,z+1/3 #7 y,-x+y,-z+1 #8 -y,x-y,z #9 x-y,x,-z+1

#10 -x+y,-x,z #11 -x,-y,-z+1 #12 -x,-y,-z #13 x-y,x,-z #14 y,-x+y,-z #15 x+1/3,y+2/3,z-1/3

Figure S1. Ball and stick structures of $(H_3O)_2Ti(IO_3)_6$. (a) The basic building unit $[Ti(IO_3)_6]^{2-}$. (b) The $[H_3O]^+$ molecule. (c) The two $[Ti(IO_3)_6]^{2-}$ units separated by two



$[H_3O]^+$ molecules. (d) The final zero-dimensional structure of $(H_3O)_2Ti(IO_3)_6$.

Figure S2. Ball and stick structures of $SrSn(IO_3)_6$. (a) The basic building unit $[Sn(IO_3)_6]^{2-}$. (b) The Sr^{2+} cation. (c) The two $[Sn(IO_3)_6]^{2-}$ units separated by one Sr^{2+} cation. (d) The final zero-dimensional structure of $SrSn(IO_3)_6$.

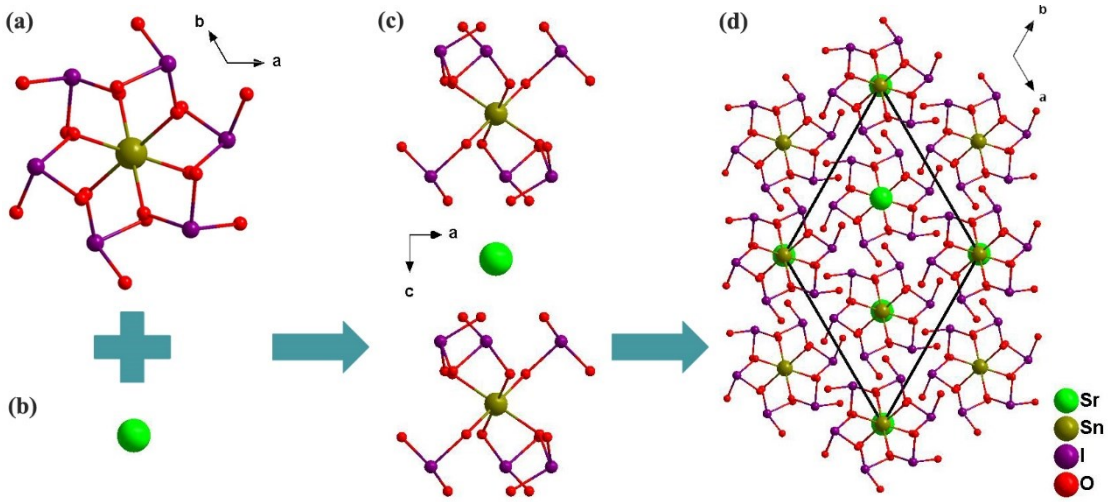


Figure S3. Distance and middle atoms of adjacent $[M(IO_3)_6]^{2-}$ (M=Ti, Sn) group in (a) $SrTi(IO_3)_6 \cdot 2H_2O$, (b) $(H_3O)_2Ti(IO_3)_6$, and (c) $SrSn(IO_3)_6$, respectively.

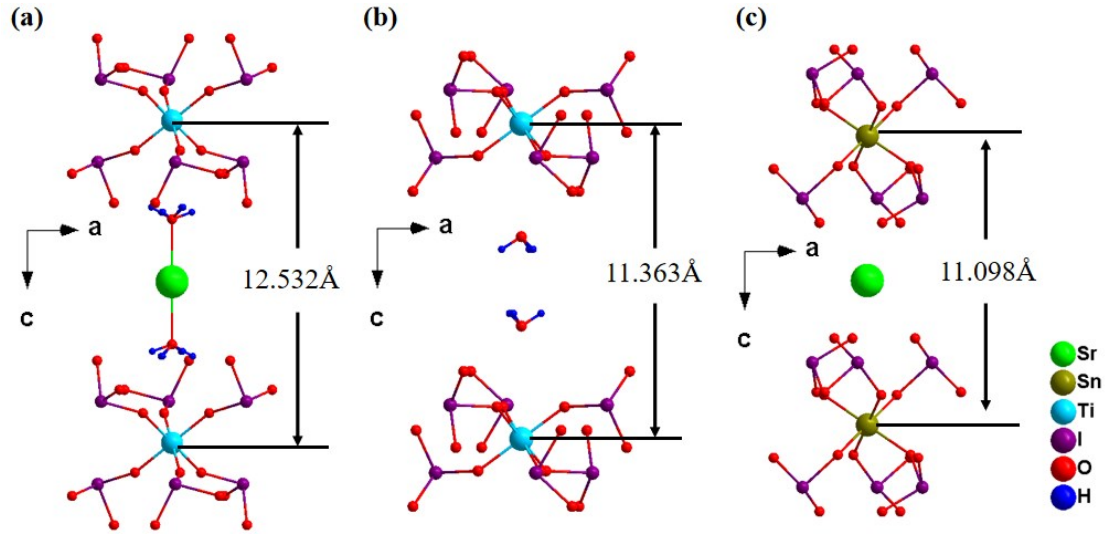


Figure S4. (a) The $[SrO_8]^{14-}$ hexagonal bipyramid in $SrTi(IO_3)_6 \cdot 2H_2O$; (b) The bipyramid with vertex Sr in $SrSn(IO_3)_6$.

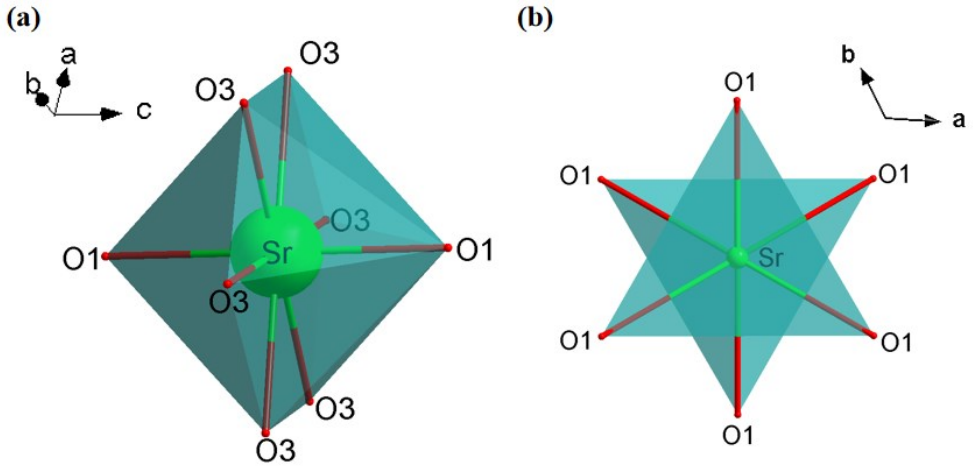


Figure S5. IR and Raman spectra of (a) $SrTi(IO_3)_6{\cdot}2H_2O$, (b) $(H_3O)_2Ti(IO_3)_6$, and (c) $SrSn(IO_3)_6$, respectively.

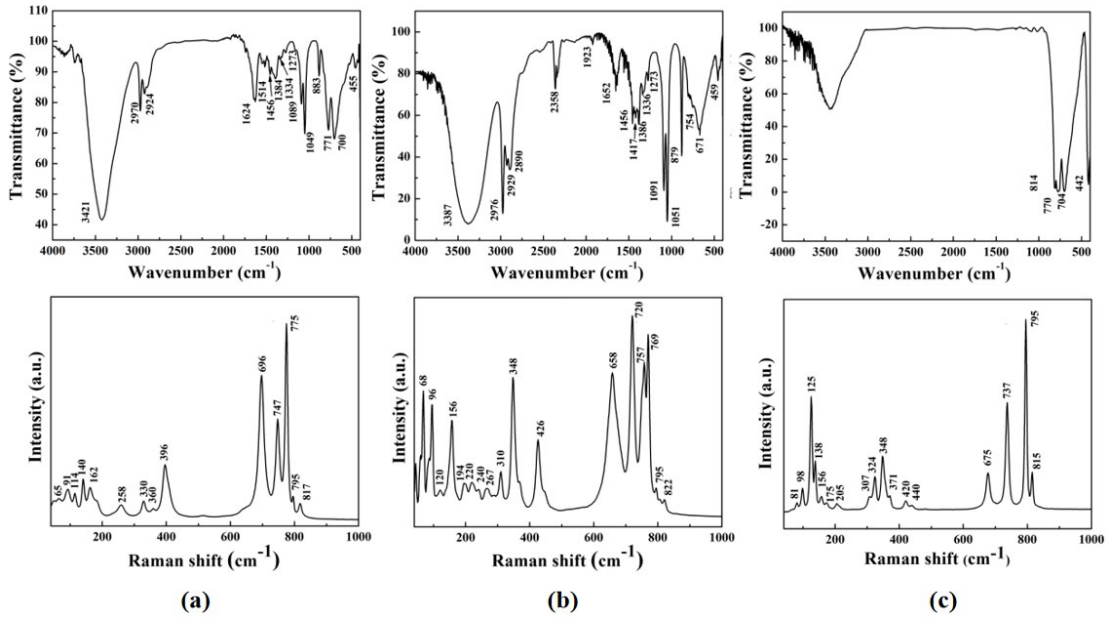


Table S3. Observed positions of the Raman bands (cm^{-1}), and proposed assignment.

$SrTi(IO_3)_6{\cdot}2H_2O$	$(H_3O)_2Ti(IO_3)_6$	$SrSn(IO_3)_6$	Proposed assignments
817, 795	822, 795	815	combination
775	769, 757	795	Antisymmetric stretching of I-O groups
747	769, 757	737	Symmetric stretching of I-O groups
696, 396	658, 426	675, 440, 420	Ti/Sn-O stretching mode
360, 330	348, 310	371, 348, 324, 307	torsional modes of Ti/Sn-O_3
258, 162, 140, 114, 91, 65	267, 240, 220, 194, 156, 120, 96, 68	205, 175, 156, 138, 125, 98, 81	Ti/Sn-O bending vibration

Figure S6. The TG-DSC curves of (a) $SrTi(IO_3)_6 \cdot 2H_2O$, (b) $(H_3O)_2Ti(IO_3)_6$, and (c) $SrSn(IO_3)_6$, respectively.

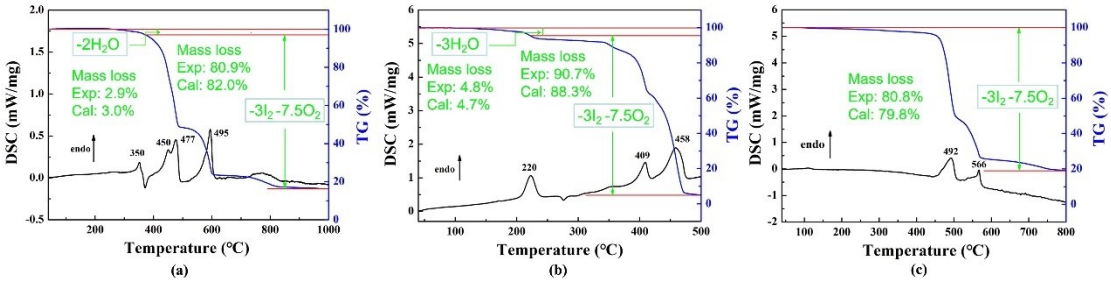


Figure S7. Room temperature magnetization plots of $SrTi(IO_3)_6 \cdot 2H_2O$, $(H_3O)_2Ti(IO_3)_6$, and $SrSn(IO_3)_6$, respectively.

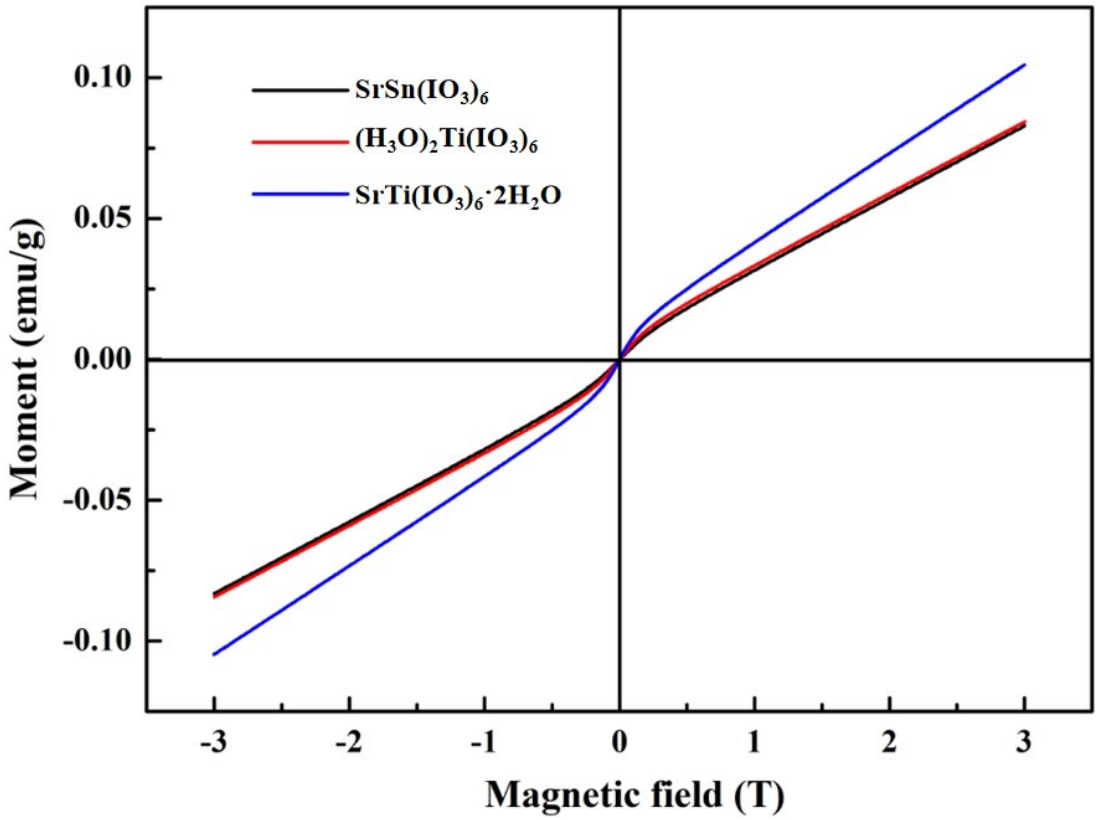


Figure S8. (a) The calculated birefringences of $SrTi(IO_3)_6{\cdot}2H_2O$, $(H_3O)_2Ti(IO_3)_6$, and $SrSn(IO_3)_6$; the contributions for birefringence of each functional groups at the static limit derived from the cut-TiO group wave functions and cut-IO group wave functions of $SrTi(IO_3)_6{\cdot}2H_2O$ (b) and $(H_3O)_2Ti(IO_3)_6$ (c).

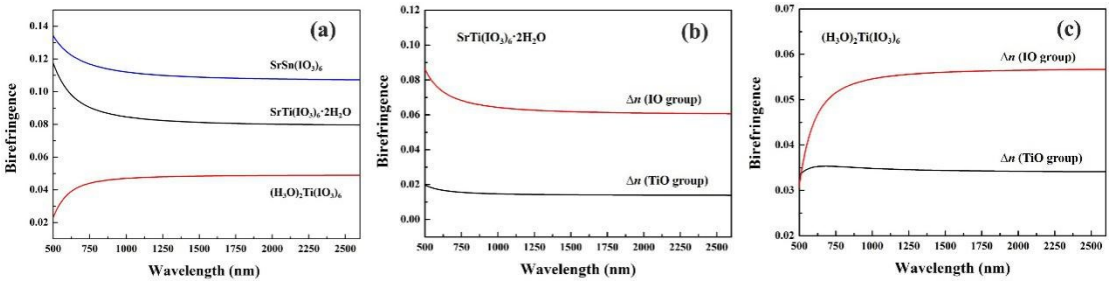


Figure S9. The arrangements diagrammatic drawing of Lone Pair Electrons of (a) $SrTi(IO_3)_6 \cdot 2H_2O$, (b) $(H_3O)_2Ti(IO_3)_6$, and (c) $SrSn(IO_3)_6$, respectively.