Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Incorporating rare-earth cations with moderate electropositivity into iodates for the optimized second-order nonlinear optical performance

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Contents

Table S1. Atomic coordinates (× 10^4), equivalent isotropic displacement parameters and bond valence sums (BVSs) for **1**−**3**.

$Y(IO_3)_3 \cdot H_2O$ (1)					
Atoms	x	y	z	U_{eq}(Å^2)	BVS
Y(1)	2595(1)	6156(1)	6925(1)	5(1)	3.16
I(1)	3374(1)	1310(1)	4638(1)	5(1)	5.03
I(2)	234(1)	889(1)	7223(1)	5(1)	5.18
I(3)	3706(1)	7590(1)	10921(1)	6(1)	5.11
O(1)	4072(8)	3262(9)	6039(6)	10(1)	1.92
O(2)	1497(8)	3258(9)	7655(7)	15(1)	2.30
O(3)	2325(8)	7694(10)	8999(5)	12(1)	2.12
O(4)	5240(7)	5118(10)	8944(5)	10(1)	2.07
O(5)	1657(8)	6563(10)	4442(6)	15(1)	2.22
O(6)	1993(8)	9686(10)	6514(6)	11(1)	2.00
O(7)	4578(7)	2454(9)	3476(6)	9(1)	2.04
O(8)	883(8)	2013(9)	3625(6)	10(1)	2.04
O(9)	1776(8)	8178(10)	11619(6)	14(1)	1.76
O(10)	2052(10)	4006(10)	763(7)	21(1)	2.36
$Eu(IO_3)_3 \cdot H_2O$ (2)					
Atoms	x	y	z	U_{eq}(Å^2)	BVS
Eu(1)	2559(1)	6142(1)	6913(1)	9(1)	3.22
I(1)	3378(1)	1326 (1)	4649(1)	9(1)	5.02
I(2)	224(1)	898(1)	7246(1)	9(1)	5.09
I(3)	3698(1)	7626(1)	10916(1)	11(1)	4.93
O(1)	4034(14)	3270(15)	6015(10)	11(2)	1.99
O(2)	1517(16)	3224(16)	7746(12)	18(2)	2.27
O(3)	2313(16)	7730(17)	9024(10)	18(2)	2.13
O(4)	5252(15)	5149(18)	8958 (10)	18(2)	2.03
O(5)	1608 (16)	6653(17)	4398(10)	18(2)	2.21
O(6)	1974(14)	9747(17)	6506(11)	14(2)	1.92
O(7)	4583(14)	2436(16)	3501(10)	12(2)	2.07
O(8)	899(15)	2020(17)	3617(11)	17(2)	2.02
O(9)	1777(17)	8226(19)	11647(12)	24(3)	1.62
O(10)	2097(17)	4010(19)	800(13)	27(3)	2.31
$La_2(IO_3)_6(H_2O)$ (3)					
Atoms	x	y	z	U_{eq}(Å^2)	BVS
La(1)	-11051(1)	-5004(1)	-7213(1)	6(1)	3.11
La(2)	-5064(1)	-173(1)	-6278(1)	6(1)	3.27
I(1)	-7572(1)	-5321(1)	-3549(1)	5(1)	4.91
I(2)	-5605(1)	-3304(1)	-5156(1)	5(1)	5.02
I(3)	-11081(1)	-1516(1)	-7198(1)	8(1)	5.03

I(4)	-10321(1)	-8123(1)	-8493(1)	7(1)	4.81
I(5)	-13371(1)	-6697(1)	-5383(1)	7(1)	5.12
I(6)	-7804(1)	1504(1)	-4830(1)	9(1)	4.94
O(1)	-8156(11)	-4594(5)	-4962(6)	14(1)	2.00
O(2)	-11220(11)	-2898(6)	-6536(6)	16(1)	2.12
O(3)	-7516(10)	-3868(5)	-6681(6)	11(1)	2.04
O(4)	-8880(10)	-4222(5)	-3115(6)	12(1)	1.97
O(5)	-3743(10)	-4558(5)	-4553(5)	10(1)	1.98
O(6)	-11654(10)	-7353(5)	-7830(5)	10(1)	1.84
O(7)	-4785(9)	-4805(6)	-2580(6)	14(1)	2.04
O(8)	-11278(10)	-6190(6)	-5622(6)	15(1)	2.09
O(9)	-11779(10)	-513(6)	-6356(7)	20(2)	2.08
O(10)	-8159(10)	-1278(5)	-6287(6)	17(1)	1.98
O(11)	-4043(9)	-2319(5)	-5527(5)	11(1)	1.99
O(12)	-7955(10)	-8605(6)	-7007(6)	17(1)	1.95
O(13)	-11761(11)	-9539(5)	-8934(6)	17(1)	1.92
O(14)	-11676(11)	-3376(5)	-8724(6)	14(1)	2.07
O(15)	-13026(10)	-8266(5)	-5533(6)	18(1)	2.18
O(16)	-5599(10)	545(6)	-4616(6)	15(1)	1.99
O(17)	-7270(11)	-1306(6)	-8291(6)	23(2)	2.00
O(18)	-6552(12)	2932(6)	-4690(7)	25(2)	1.73
O(19)	-5310(11)	1188(6)	-8069(6)	23(2)	2.59

Table S2. Selected bond distances (Å) and angles (°) for **1**−**3**.[a]

$Y(IO_3)_3 \cdot H_2O$ (1)			
I(1)-O(1)	1.821(6)	O(2)-Y(1)-O(3)	87.0(2)
I(1)-O(7)	1.816(5)	O(5)-Y(1)-O(3)	141.7(2)
I(1)-O(8)	1.799(5)	O(2)-Y(1)-O(4)	76.2(2)
I(2)-O(2)	1.785(6)	O(5)-Y(1)-O(4)	142.0(2)
I(2)-O(5)#1	1.793(6)	O(3)-Y(1)-O(4)	71.19(19)
I(2)-O(6)#2	1.826(5)	O(2)-Y(1)-O(7)#4	140.2(2)
I(3)-O(3)	1.808(5)	O(5)-Y(1)-O(7)#4	75.2(2)
I(3)-O(4)#3	1.817(6)	O(3)-Y(1)-O(7)#4	108.7(2)
I(3)-O(9)	1.794(6)	O(4)-Y(1)-O(7)#4	74.94(19)
Y(1)-O(1)	2.482(6)	O(2)-Y(1)-O(6)	144.2(2)
Y(1)-O(2)	2.274(6)	O(5)-Y(1)-O(6)	74.7(2)
Y(1)-O(3)	2.338(5)	O(3)-Y(1)-O(6)	70.0(2)
Y(1)-O(4)	2.340(5)	O(4)-Y(1)-O(6)	118.7(2)
Y(1)-O(5)	2.308(5)	O(7)#4-Y(1)-O(6)	74.8(2)
Y(1)-O(6)	2.373(6)	O(2)-Y(1)-O(8)#5	79.6(2)
Y(1)-O(7)#4	2.372(5)	O(5)-Y(1)-O(8)#5	80.2(2)
Y(1)-O(8)#5	2.456(5)	O(3)-Y(1)-O(8)#5	73.05(18)
O(10)-H(1A)	0.820(10)	O(4)-Y(1)-O(8)#5	137.42(18)
O(10)-H(1B)	0.820(10)	O(7)#4-Y(1)-O(8)#5	139.47(19)
O(8)-I(1)-O(7)	98.7(2)	O(6)-Y(1)-O(8)#5	67.81(19)
O(8)-I(1)-O(1)	101.8(3)	O(2)-Y(1)-O(1)	72.8(2)
O(7)-I(1)-O(1)	96.3(3)	O(5)-Y(1)-O(1)	74.2(2)
O(2)-I(2)-O(5)#1	99.9(3)	O(3)-Y(1)-O(1)	144.08(18)
O(2)-I(2)-O(6)#2	95.8(3)	O(4)-Y(1)-O(1)	75.23(18)
O(5)#1-I(2)-O(6)#2	100.2(3)	O(7)#4-Y(1)-O(1)	73.72(19)
O(9)-I(3)-O(3)	99.3(3)	O(6)-Y(1)-O(1)	140.24(19)
O(9)-I(3)-O(4)#3	97.9(3)	O(8)#5-Y(1)-O(1)	129.17(18)
O(3)-I(3)-O(4)#3	96.4(3)	H(1A)-O(10)-H(1B)	116(2)
O(2)-Y(1)-O(5)	114.8(2)		
$Eu(IO_3)_3 \cdot H_2O$ (2)			
I(1)-O(8)	1.812(10)	Eu(1)-O(3)	2.399(10)
I(1)-O(7)	1.812(9)	Eu(1)-O(4)	2.388(10)
I(1)-O(1)	1.812(9)	Eu(1)-O(5)	2.369(10)
I(2)-O(2)	1.791(11)	Eu(1)-O(6)	2.441(11)
I(2)-O(5)#6	1.793(10)	Eu(1)-O(7)#1	2.416(10)
I(2)-O(6)#7	1.840(10)	Eu(1)-O(8)#2	2.470(11)
I(3)-O(3)	1.804(9)	O(10)-H(1A)	0.8281
I(3)-O(4)#8	1.829(12)	O(10)-H(1B)	0.8278
I(3)-O(9)	1.825(11)	O(8)-I(1)-O(7)	98.5(5)
Eu(1)-O(1)	2.497(10)	O(8)-I(1)-O(1)	101.6(5)
Eu(1)-O(2)	2.332(11)	O(7)-I(1)-O(1)	96.6(5)

O(2)-I(2)-O(5)#6	99.9(5)	O(4)-Eu(1)-O(6)	117.3(4)
O(2)-I(2)-O(6)#7	95.5(5)	O(3)-Eu(1)-O(6)	69.6(4)
O(5)#6-I(2)-O(6)#7	99.3(5)	O(7)#1-Eu(1)-O(6)	74.7(3)
O(3)-I(3)-O(9)	99.5(5)	O(2)-Eu(1)-O(8)#2	80.7(4)
O(3)-I(3)-O(4)#8	96.3(5)	O(5)-Eu(1)-O(8)#2	80.1(4)
O(9)-I(3)-O(4)#8	97.7(5)	O(4)-Eu(1)-O(8)#2	137.3(4)
O(2)-Eu(1)-O(5)	118.3(4)	O(3)-Eu(1)-O(8)#2	73.1(3)
O(2)-Eu(1)-O(4)	75.2(4)	O(7)#1-Eu(1)-O(8)#2	139.5(4)
O(5)-Eu(1)-O(4)	142.5(4)	O(6)-Eu(1)-O(8)#2	67.9(4)
O(2)-Eu(1)-O(3)	85.9(4)	O(2)-Eu(1)-O(1)	73.9(3)
O(5)-Eu(1)-O(3)	140.2(4)	O(5)-Eu(1)-O(1)	75.2(4)
O(4)-Eu(1)-O(3)	70.6(4)	O(4)-Eu(1)-O(1)	76.1(3)
O(2)-Eu(1)-O(7)#1	139.4(4)	O(3)-Eu(1)-O(1)	144.4(3)
O(5)-Eu(1)-O(7)#1	74.6(4)	O(7)#1-Eu(1)-O(1)	73.2(3)
O(4)-Eu(1)-O(7)#1	74.4(4)	O(6)-Eu(1)-O(1)	139.7(3)
O(3)-Eu(1)-O(7)#1	108.3(4)	O(8)#2-Eu(1)-O(1)	129.6(3)
O(2)-Eu(1)-O(6)	144.4(3)	H(1A)-O(10)-H(1B)	116.1
O(5)-Eu(1)-O(6)	73.4(4)		

$La_2(IO_3)_6(H_2O)$ (3)

I(1)-O(7)	1.816(6)	La(1)-O(14)	2.512(7)
I(1)-O(1)	1.817(7)	La(1)-O(6)	2.703(6)
I(1)-O(4)	1.821(6)	La(2)-O(15)#3	2.478(6)
I(2)-O(3)	1.796(7)	La(2)-O(9)#4	2.483(7)
I(2)-O(5)	1.811(6)	La(2)-O(12)#5	2.501(7)
I(2)-O(11)	1.821(6)	La(2)-O(16)	2.513(6)
I(3)-O(2)	1.794(6)	La(2)-O(17)	2.525(7)
I(3)-O(9)	1.816(7)	La(2)-O(11)	2.545(6)
I(3)-O(10)	1.817(7)	La(2)-O(10)	2.571(6)
I(4)-O(13)	1.810(7)	La(2)-O(19)	2.676(7)
I(4)-O(6)	1.825(6)	La(2)-O(13)#6	2.685(7)
I(4)-O(12)	1.841(7)	O(19)-H(1A)	0.8229
I(5)-O(15)	1.794(6)	O(19)-H(1B)	0.8241
I(5)-O(8)	1.802(6)	O(7)-I(1)-O(4)	98.9(3)
I(5)-O(14)#7	1.810(7)	O(7)-I(1)-O(1)	96.7(3)
I(6)-O(18)	1.798(7)	O(4)-I(1)-O(1)	97.3(3)
I(6)-O(17)#8	1.822(7)	O(3)-I(2)-O(5)	99.1(3)
I(6)-O(16)	1.827(6)	O(3)-I(2)-O(11)	98.6(3)
La(1)-O(7)#1	2.512(6)	O(5)-I(2)-O(11)	98.5(3)
La(1)-O(8)	2.527(6)	O(2)-I(3)-O(9)	98.1(3)
La(1)-O(2)	2.539(7)	O(2)-I(3)-O(10)	99.6(3)
La(1)-O(1)	2.550(7)	O(9)-I(3)-O(10)	97.7(3)
La(1)-O(4)#2	2.566(6)	O(13)-I(4)-O(6)	101.1(3)
La(1)-O(5)#1	2.599(6)	O(13)-I(4)-O(12)	97.6(3)
La(1)-O(3)	2.615(6)	O(6)-I(4)-O(12)	95.1(3)

O(15)-I(5)-O(14)#7	97.2(3)	O(18)-I(6)-O(16)	98.4(3)
O(15)-I(5)-O(8)	96.1(3)	O(17)#8-I(6)-O(16)	96.4(3)
O(14)#7-I(5)-O(8)	94.9(3)	H(1A)-O(19)-H(1B)	115.1
O(18)-I(6)-O(17)#8	101.6(3)		

[a]Symmetry codes:

1: #1 -x, y-1/2, -z+1; #2 x, y-1, z; #3 -x+1, y+1/2, -z+2; #4 -x+1, y+1/2, -z+1; #5 -x, y+1/2, -z+1.

2: #1 -x+1,y+1/2,-z+1; #2 -x,y+1/2,-z+1; #3 x,y+1,z; #4 -x+1,y-1/2,-z+2, #5 -x+1,y-1/2,-z+1, #6 -x,y-1/2,-z+1, #7 x,y-1,z, #8 -x+1,y+1/2,-z+2.

3: #1 x-1, -y-1, z-1/2; #2 x, -y-1, z-1/2; #3 x+1, y+1, z; #4 x+1, y, z; #5 x, y+1, z; #6 x+1, -y-1, z+1/2; #7 x, -y-1, z+1/2; #8 x, -y, z+1/2.

Table S3. Hydrogen bond distances (Å) and angles (°) for **1**−**3**.

$Y(IO_3)_3·H_2O$ (1)				
D-H···A	D-H	H···A	D···A	D-H···A
O10-H1A···O2	0.8200	2.5800	2.9741	111.00
O10-H1A···O9	0.8200	2.1900	3.0057	177.00
O10-H1B···O7	0.8200	2.2200	2.8545	134.00
O10-H1B···O4	0.8200	2.4600	3.1778	147.00
$Eu(IO_3)_3·H_2O$ (2)				
D-H···A	D-H	H···A	D···A	D-H···A
O10-H1A···O2	0.8281	2.5400	2.9504	112.00
O10-H1A···O9	0.8281	2.2600	3.0824	176.00
O10-H1B···O4	0.8278	2.4500	3.1733	146.00
O10-H1B···O7	0.8278	2.2300	2.8713	134.00
$La_2(IO_3)_6(H_2O)$ (3)				
D-H···A	D-H	H···A	D···A	D-H···A
O19-H1A···O6	0.8229	2.2900	2.9979	145.00
O19-H1B···I6	0.8241	2.9100	3.6109	144.00
O19-H1B···O16	0.8241	1.8800	2.7041	178.00

Table S4. Comparison of the optical properties of rare-earth iodate crystals.

Compound	Space group	SHG @1064 nm	Band gap (eV)
$NaLa(IO_3)_4$[1]	*Cc*	120 × α-SiO_2@1064 nm	4.16
$NaCe(IO_3)_4$[1]	*Cc*	50 × α-SiO_2@1064 nm	2.97
$NaSm(IO_3)_4$[1]	*Cc*	60 × α-SiO_2@1064 nm	4.01
$NaEu(IO_3)_4$[1]	*Cc*	130 × α-SiO_2@1064 nm	4.16
$La_3(IO_3)_8(OH)$[2]	*P*3c1	0.6 × KDP@1064 nm	4.34
$La(IO_3)_2(NO_3)$[2]	$P3_121$	-	4.23
$Ce_2I_6O_{18}$[3]	$P2_1$	9 × KDP@1064 nm	2.5
$K_8Ce_2I_{18}O_{53}$[4]	*C*2/*c*	-	2.34
$Ce(IO_3)_2F_2·H_2O$[5]	*Ima*2	3 × KDP@1064 nm	2.6
$Ce_2(IO_3)_8(H_2O)$[6]	*R*3*c*	9.2 × KDP@1064 nm	2.43
$Ce(MoO_2)(IO_3)_4(OH)$[7]	$P2_1$	-	2.41
$Y(IO_3)_3(H_2O)$[a]	$P2_1$	3 × KDP@1064 nm	4.12
$Eu(IO_3)_3(H_2O)$[a]	$P2_1$	4.5 × KDP@1064 nm	4.36
$La_2(IO_3)_6(H_2O)$[a]	*Pc*	1.5 × KDP@1064 nm	4.24

"-" means crystal has no SHG signal or shows negligible measurable SHG activity. [a] This work

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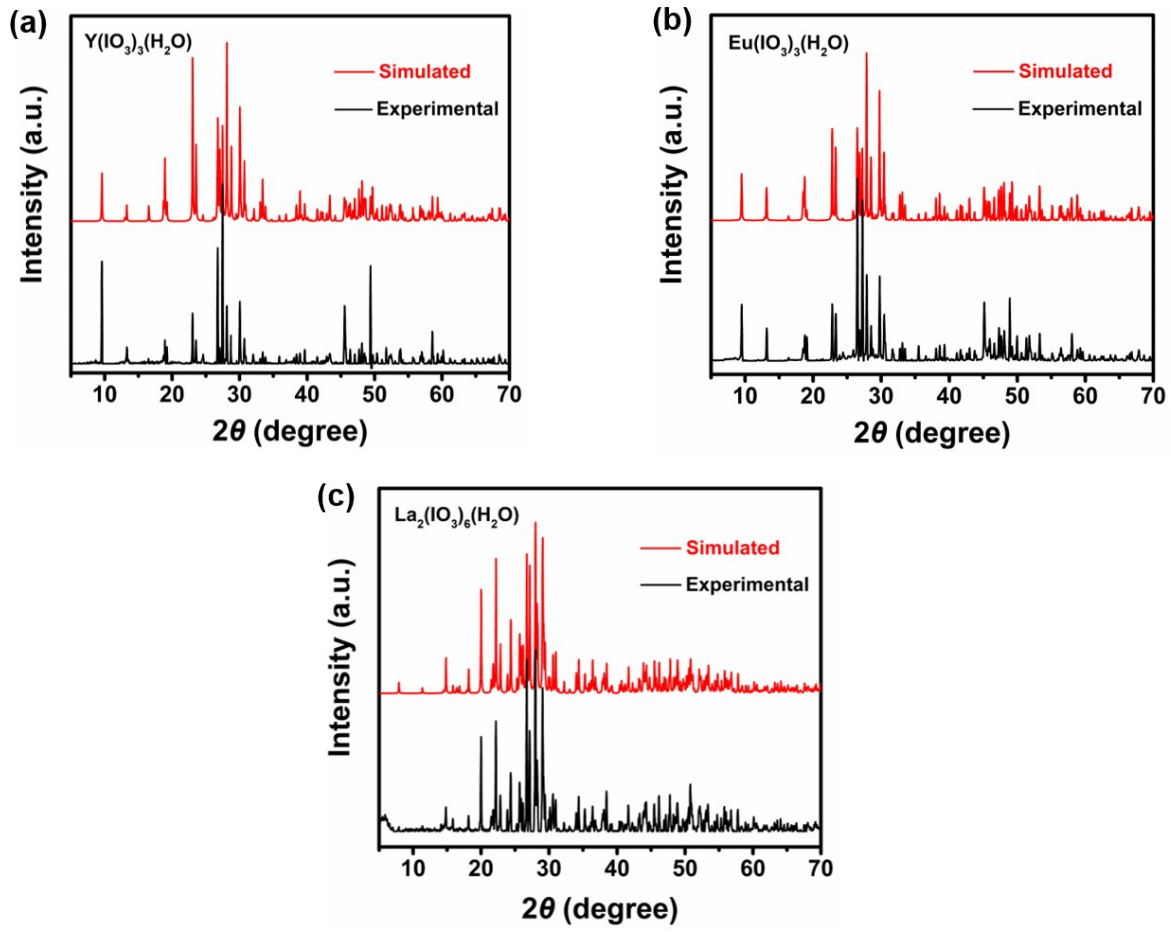

Figure S1. Experimental and simulated powder X-ray diffraction (PXRD) patterns of **1** (a), **2** (b), and **3** (c).

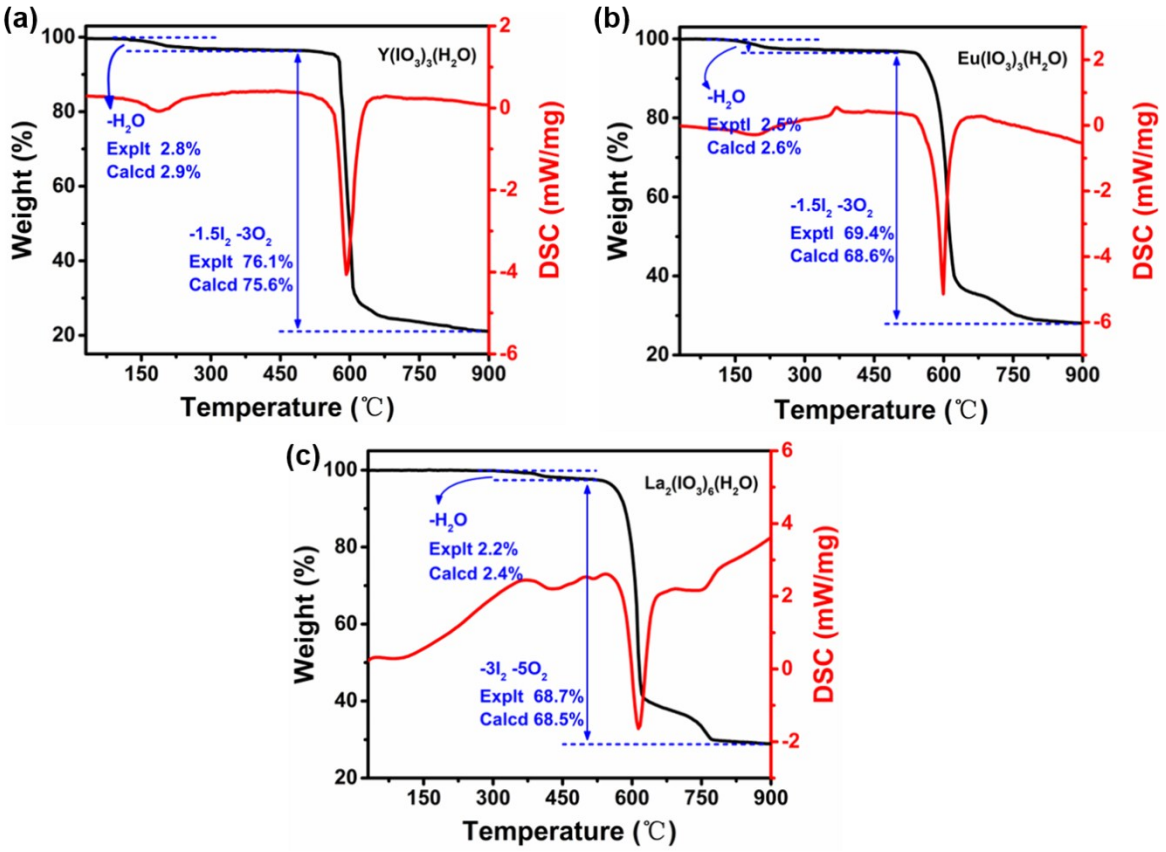

Figure S2. Thermogravimetric analyses of **1** (a), **2** (b), and **3** (c) under a nitrogen atmosphere.

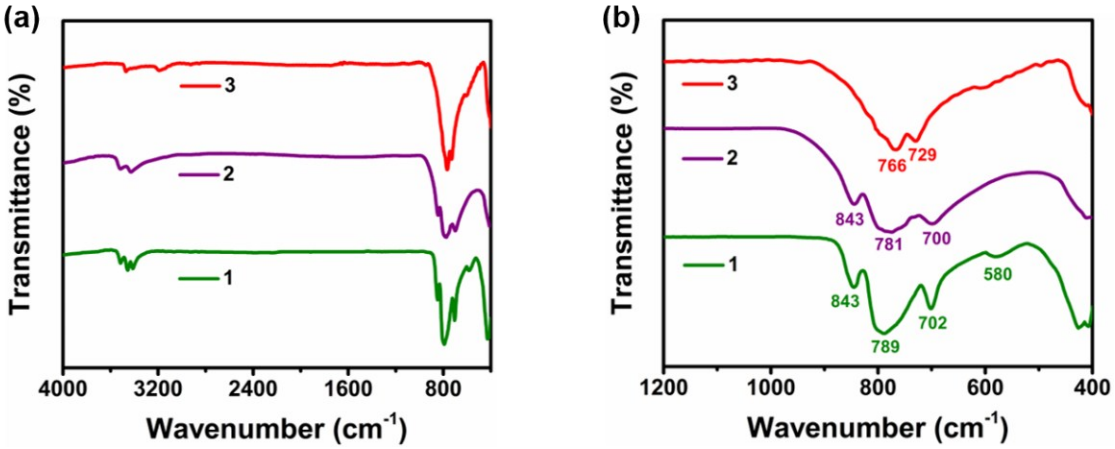

Figure S3. Infrared transmittance spectra of **1**−**3**.

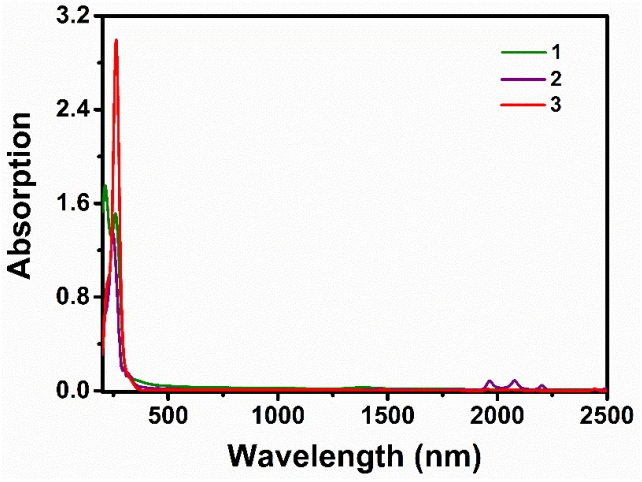

Figure S4. Ultraviolet (UV) absorption spectra of **1**−**3**.

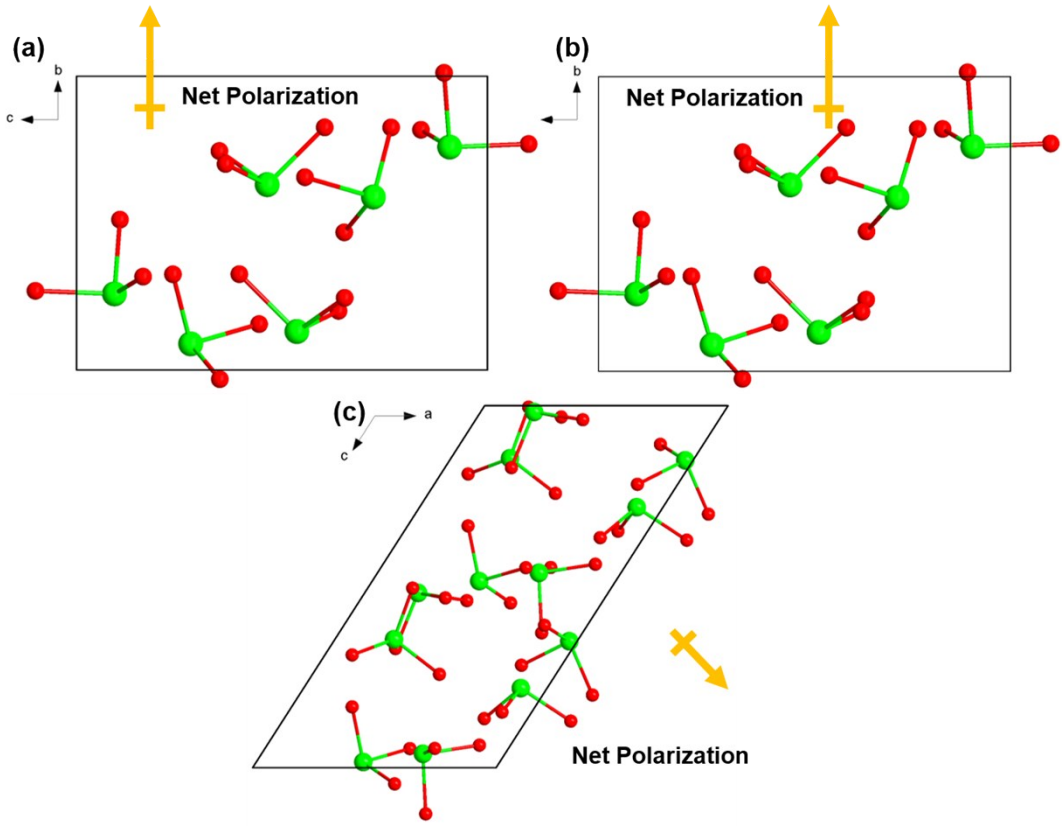

Figure S5. Net polarizations in the unit cells of **1** (a), **2** (b), and **3** (c).

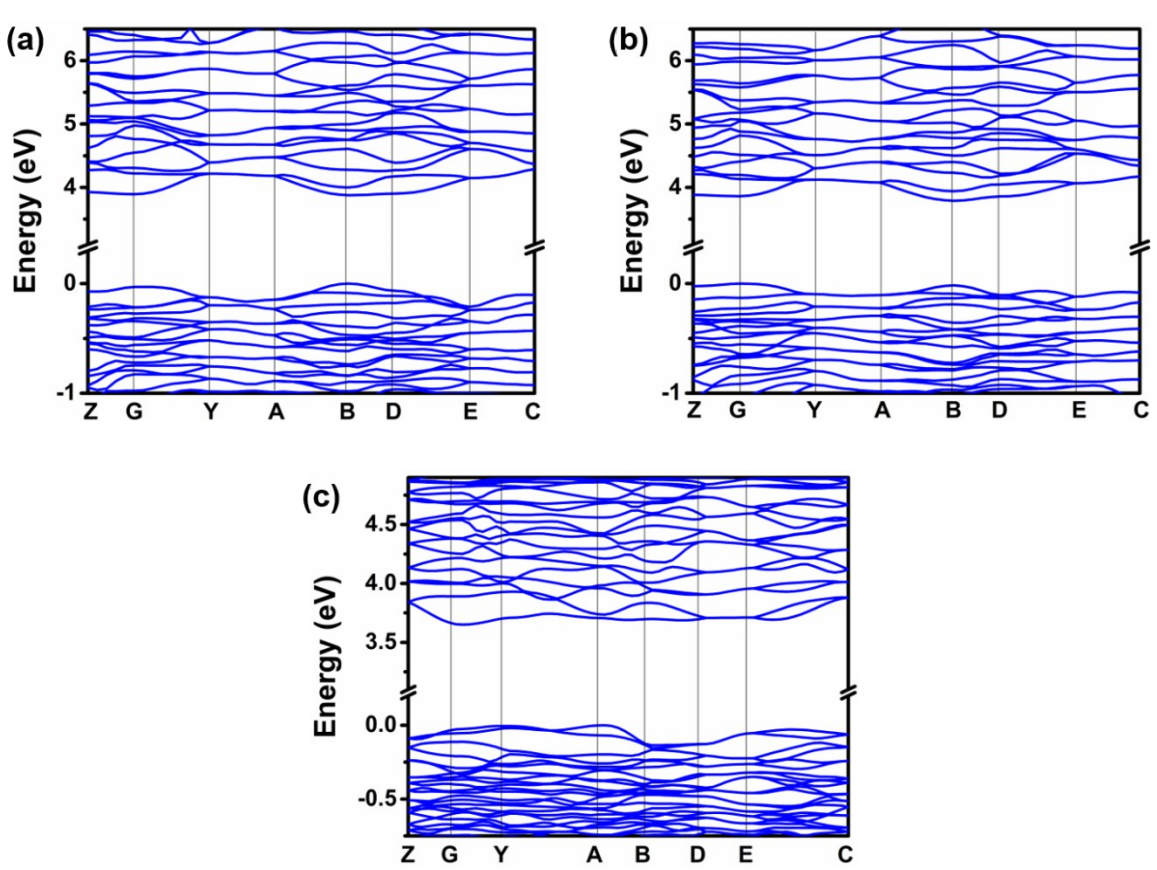

Figure S6. Calculated band structures of **1** (a), **2** (b), and **3** (c).

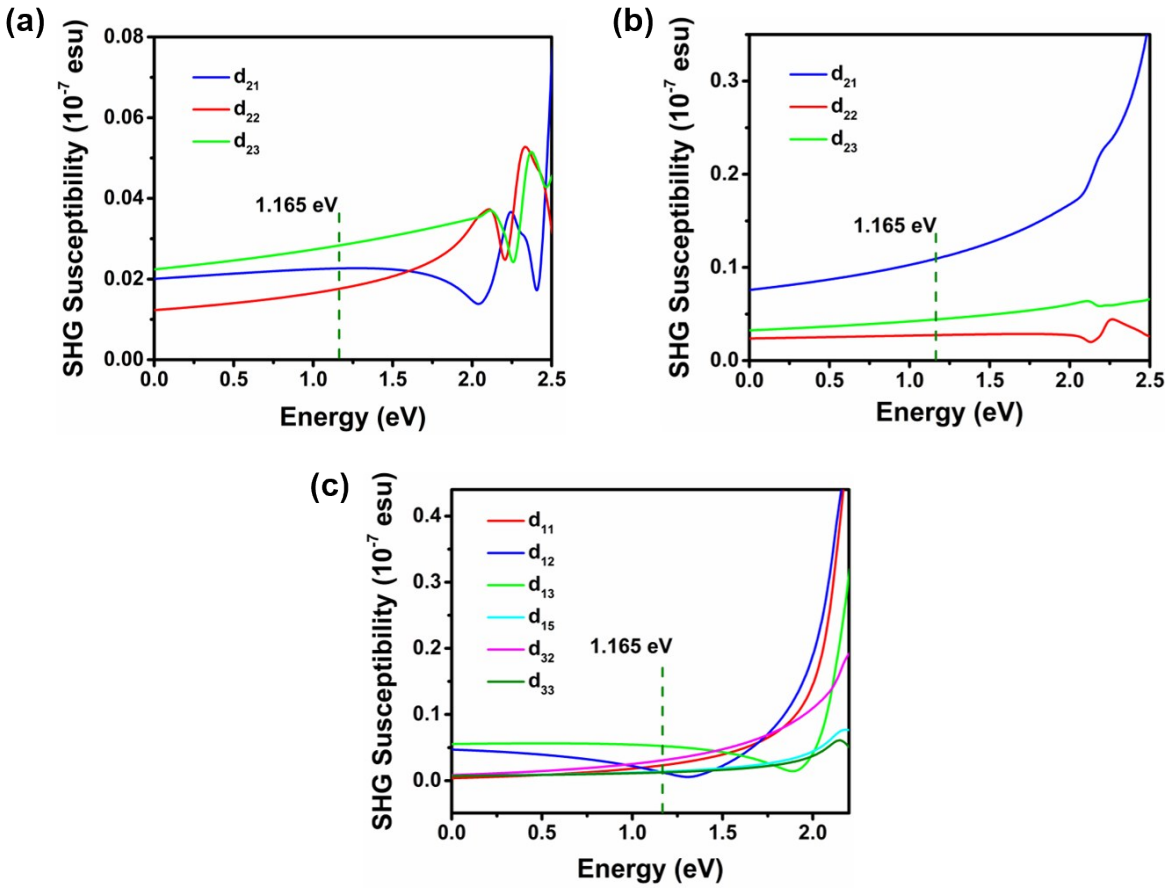

Figure S7. Frequency-dependent SHG susceptibilities of **1** (a), **2** (b), and **3** (c).