Supporting Information

Experimental and ab Initio Studies of Two UV Nonlinear Optical Materials

Juanjuan Lu,[†,‡] Guoqiang Shi,[†,‡] Hongping Wu,[*,†] Ming Wen,[c] Dianwei Hou,[†] Zhihua Yang,[†] Fangfang Zhang,[*,†] Shilie Pan[*,†]

[†] JJ and GQ contributed equally

[†]*Key Laboratory of Functional Materials and Devices for Special Environments of CAS; Xinjiang Key Laboratory of Electronic Information Materials and Devices; Xinjiang Technical Institute of Physics & Chemistry of CAS, 40-1 South Beijing Road, Urumqi 830011, China*

[‡]*University of Chinese Academy of Sciences, Beijing 100049, China*

[c]*School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin Heilongjiang 150001, China.*

*To whom correspondence should be addressed. Phone: (+86)991-3674558.

Fax: (+86)991-3838957. E-mail: slpan@ms.xjb.ac.cn (S. Pan).

Table S1. Atomic coordinates (× 10^4), equivalent isotropic displacement coefficients ($Å^2$ × 10^3) and BVS for compounds **I**, **II** and **III.**

Compound **I**					
Atom	X	y	z	$U_{(eq)}$[a]	BVS[b,c]
Ba(1)	3994(3)	1248(2)	5301(2)	15(1)	2.40
Ba(2)	3360(20)	922(15)	5386(12)	15(1)	2.13
B(1)	3058(14)	4335(15)	6193(16)	12(3)	2.77
B(2)	3965(15)	4303(13)	3529(15)	9(2)	3.11
B(3)	5019(15)	2092(15)	8924(16)	12(3)	2.99
B(4)	0	0	3430(60)	59(12)	3.20
O(1)	3932(8)	3992(8)	5216(8)	6(2)	2.23
O(2)	2713(9)	-1941(9)	5577(9)	10(2)	2.17
O(3)	4066(9)	2503(9)	8042(9)	10(2)	2.27
O(4)	4162(8)	-698(8)	3278(8)	8(2)	2.03
O(5)	4298(8)	3213(8)	2766(8)	7(2)	2.09
O(6)	6667	3333	8723(15)	6(3)	1.92
O(7)	1240(11)	-136(11)	3464(17)	51(4)	2.21
O(8)	6667	3333	5190(20)	29(4)	2.49
Compound **II**					
Atom	X	y	z	$U_{(eq)}$	BVS
$Ba_{0.72}Pb_{0.28}$	5956(1)	7250(1)	7350(2)	23(1)	1.90
B(1)	8702(18)	5686(19)	8260(20)	17(4)	2.95
B(2)	4965(18)	7064(17)	10930(20)	18(3)	2.99
B(3)	3940(20)	4260(20)	10580(20)	26(4)	3.05
B(4)	10000	10000	5540(50)	32(8)	3.02
O(1)	3333	6667	7160(30)	25(5)	2.17
O(2)	8721(14)	8612(15)	5450(20)	49(4)	2.13
O(3)	6123(11)	10061(12)	7242(12)	21(3)	2.05
O(4)	5941(12)	8426(11)	10054(13)	19(3)	1.98

O(5)	7323(12)	5337(12)	7610(12)	21(3)	1.88
O(6)	3333	6667	10730(18)	10(3)	2.03
O(7)	5147(11)	5834(11)	10283(12)	14(2)	2.04
O(8)	8895(12)	5709(12)	9791(12)	16(2)	2.09

Compound **III**

Atom	X	y	z	$U_{(eq)}$[a]	BVS[b,c]
Pb(1)	8652(1)	2729(1)	7855(1)	16(1)	1.95
B(1)	5772(10)	-287(10)	6004(10)	8(2)	3.07
B(2)	4966(10)	-2964(10)	6354(10)	7(2)	3.05
B(3)	5696(10)	-1297(10)	8676(11)	9(2)	2.96
B(4)	10000	10000	6060(30)	26(4)	3.11
O(1)	5317(6)	-2712(6)	8044(7)	6(1)	1.82
O(2)	5964(6)	-1570(6)	5484(6)	7(1)	1.89
O(3)	3333	-3333	6113(10)	6(2)	2.07
O(4)	6103(6)	-50(6)	7708(7)	12(1)	2.00
O(5)	6859(6)	1139(6)	5257(7)	9(1)	2.00
O(6)	5177(6)	-4182(6)	5745(7)	8(1)	1.93
O(7)	6667	3333	7424(12)	15(2)	2.29
O(8)	8641(8)	8666(8)	6078(10)	37(2)	2.09

[a] $U_{(eq)}$ is defined as the one-third of the trace of the orthogonalized U_{ij} tensor;

[b] Bond valences calculated with the program Bond Valence Calculator Version 2.00, C. Hormillosa, S. Healy, T. Stephen, McMaster University, 1993;

[c] Valence sums calculated with the formula: $S_i = \exp[(R_0-R_i)/B]$, where S_i = valence of bond ‘‘i’’ and B = 0.37.

Table S2a. Selected bond lengths (Å) and angels (deg) for compound **I**.

Ba(1)-O(3)	2.675(8)	O(3)-Ba(1)-O(1)#2	112.4(2)
Ba(1)-O(4)	2.719(8)	O(4)-Ba(1)-O(1)#2	48.7(2)
Ba(1)-O(1)	2.846(7)	O(1)-Ba(1)-O(1)#2	144.0(2)
Ba(1)-O(2)	2.860(8)	O(2)-Ba(1)-O(1)#2	60.8(2)
Ba(1)-O(4)#1	2.864(7)	O(4)#1-Ba(1)-O(1)#2	65.1(2)
Ba(1)-O(5)	2.882(7)	O(5)-Ba(1)-O(1)#2	116.1(2)
Ba(1)-O(7)	2.913(12)	O(7)-Ba(1)-O(1)#2	119.3(2)
Ba(1)-O(1)#2	2.973(7)	O(7)-Ba(2)-O(2)	83.1(5)
Ba(2)-O(7)	2.507(18)	O(7)-Ba(2)-O(3)	137.6(7)
Ba(2)-O(2)	2.672(14)	O(2)-Ba(2)-O(3)	117.0(4)
Ba(2)-O(3)	2.687(13)	O(7)-Ba(2)-O(4)	76.5(4)
Ba(2)-O(4)	2.847(14)	O(2)-Ba(2)-O(4)	51.9(3)
Ba(2)-O(1)	2.902(14)	O(3)-Ba(2)-O(4)	145.7(6)
Ba(2)-O(4)#1	3.000(13)	O(7)-Ba(2)-O(1)	95.6(4)
Ba(2)-O(8)	3.043(18)	O(2)-Ba(2)-O(1)	177.6(7)
Ba(2)-O(5)	3.047(14)	O(3)-Ba(2)-O(1)	62.7(3)
Ba(2)-O(7)#1	3.192(19)	O(4)-Ba(2)-O(1)	129.8(5)
B(1)-O(5)#4	1.368(15)	O(7)-Ba(2)-O(4)#1	152.0(7)
B(1)-O(1)	1.397(14)	O(2)-Ba(2)-O(4)#1	73.7(3)
B(1)-O(2)#5	1.441(15)	O(3)-Ba(2)-O(4)#1	49.0(3)
B(2)-O(4)#6	1.442(14)	O(4)-Ba(2)-O(4)#1	100.2(5)
B(2)-O(3)#7	1.456(15)	O(1)-Ba(2)-O(4)#1	107.0(4)
B(2)-O(5)	1.476(14)	O(7)-Ba(2)-O(8)	133.4(6)
B(2)-O(1)	1.486(15)	O(2)-Ba(2)-O(8)	117.3(5)
B(3)-O(3)	1.457(15)	O(3)-Ba(2)-O(8)	72.8(5)
B(3)-O(2)#1	1.462(16)	O(4)-Ba(2)-O(8)	84.7(5)
B(3)-O(4)#1	1.465(15)	O(1)-Ba(2)-O(8)	65.0(3)
B(3)-O(6)	1.534(13)	O(4)#1-Ba(2)-O(8)	72.7(5)

B(4)-O(7)#8	1.347(10)	O(7)-Ba(2)-O(5)	73.5(4)
B(4)-O(7)#5	1.347(10)	O(2)-Ba(2)-O(5)	134.6(4)
B(4)-O(7)	1.347(9)	O(3)-Ba(2)-O(5)	106.3(5)
O(8)-Ba(1)-O(3)	82.5(4)	O(4)-Ba(2)-O(5)	84.5(4)
O(8)-Ba(1)-O(4)	99.1(3)	O(1)-Ba(2)-O(5)	46.5(3)
O(3)-Ba(1)-O(4)	157.4(2)	O(4)#1-Ba(2)-O(5)	134.3(6)
O(8)-Ba(1)-O(1)	73.14(14)	O(8)-Ba(2)-O(5)	62.4(4)
O(3)-Ba(1)-O(1)	63.7(2)	O(7)-Ba(2)-O(7)#1	97.8(6)
O(4)-Ba(1)-O(1)	138.6(2)	O(2)-Ba(2)-O(7)#1	84.0(4)
O(8)-Ba(1)-O(2)	131.48(18)	O(3)-Ba(2)-O(7)#1	52.4(3)
O(3)-Ba(1)-O(2)	111.3(2)	O(4)-Ba(2)-O(7)#1	135.8(5)
O(4)-Ba(1)-O(2)	51.4(2)	O(1)-Ba(2)-O(7)#1	94.2(4)
O(1)-Ba(1)-O(2)	155.2(2)	O(4)#1-Ba(2)-O(7)#1	64.9(3)
O(8)-Ba(1)-O(4)#1	83.6(4)	O(5)-Ba(2)-O(7)#1	136.7(5)
O(3)-Ba(1)-O(4)#1	50.6(2)	O(5)#4-B(1)-O(1)	119.5(10)
O(4)-Ba(1)-O(4)#1	106.91(19)	O(5)#4-B(1)-O(2)#5	119.2(10)
O(1)-Ba(1)-O(4)#1	112.3(2)	O(1)-B(1)-O(2)#5	121.2(11)
O(2)-Ba(1)-O(4)#1	73.2(2)	O(4)#6-B(2)-O(3)#7	111.6(9)
O(8)-Ba(1)-O(5)	71.5(4)	O(4)#6-B(2)-O(5)	112.1(9)
O(3)-Ba(1)-O(5)	111.5(2)	O(3)#7-B(2)-O(5)	110.7(9)
O(4)-Ba(1)-O(5)	90.1(2)	O(4)#6-B(2)-O(1)	107.3(9)
O(1)-Ba(1)-O(5)	48.5(2)	O(3)#7-B(2)-O(1)	109.6(9)
O(2)-Ba(1)-O(5)	133.6(2)	O(5)-B(2)-O(1)	105.3(9)
O(4)#1-Ba(1)-O(5)	151.9(2)	O(3)-B(3)-O(2)#1	111.5(9)
O(8)-Ba(1)-O(7)	141.0(5)	O(2)#1-B(3)-O(4)#1	111.7(10)
O(3)-Ba(1)-O(7)	120.1(3)	O(3)-B(3)-O(6)	108.7(10)
O(4)-Ba(1)-O(7)	72.3(3)	O(2)#1-B(3)-O(6)	108.4(10)
O(2)-Ba(1)-O(7)	73.1(3)	O(4)#1-B(3)-O(6)	107.8(9)
O(4)#1-Ba(1)-O(7)	135.4(3)	O(7)#8-B(4)-O(7)#5	119.9(2)

O(5)-Ba(1)-O(7)	70.6(3)	O(7)#8-B(4)-O(7)	119.9(2)
O(8)-Ba(1)-O(1)#2	70.90(16)	O(7)#5-B(4)-O(7)	119.9(2)

Symmetry transformations used to generate equivalent atoms:

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

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

#7 y,x,z-1/2 #8 -x+y,-x,z

Table S2b. Selected bond lengths (Å) and angels (deg) for compound **II**.

Ba/Pb-O(1)	2.442(3)	O(7)-Ba/Pb-O(8)#1	154.4(3)
Ba/Pb-O(4)	2.619(11)	O(1)-Ba/Pb-O(5)	132.4(2)
Ba/Pb-O(7)#1	2.741(10)	O(4)-Ba/Pb-O(5)	110.7(3)
Ba/Pb-O(3)	2.793(12)	O(7)#1-Ba/Pb-O(5)	51.3(3)
Ba/Pb-O(7)	2.815(11)	O(3)-Ba/Pb-O(5)	152.4(3)
Ba/Pb-O(8)#1	2.853(11)	O(7)-Ba/Pb-O(5)	72.8(3)
Ba/Pb-O(5)	2.924(12)	O(8)#1-Ba/Pb-O(5)	131.7(3)
Ba/Pb-O(2)	2.939(14)	O(1)-Ba/Pb-O(2)	139.1(6)
Ba/Pb-O(3)#2	3.005(10)	O(4)-Ba/Pb-O(2)	119.9(4)
Ba/Pb-B(2)	3.211(18)	O(7)#1-Ba/Pb-O(2)	70.7(4)
Ba/Pb-B(3)#1	3.296(19)	O(3)-Ba/Pb-O(2)	86.8(4)
Ba/Pb-B(2)#1	3.296(18)	O(7)-Ba/Pb-O(2)	134.8(4)
B(1)-O(8)	1.33(2)	O(8)#1-Ba/Pb-O(2)	69.0(4)
B(1)-O(5)	1.39(2)	O(5)-Ba/Pb-O(2)	72.0(4)
B(1)-O(3)#3	1.423(19)	O(1)-Ba/Pb-O(3)#2	71.2(2)
B(2)-O(4)	1.45(2)	O(4)-Ba/Pb-O(3)#2	113.3(3)
B(2)-O(7)	1.467(18)	O(7)#1-Ba/Pb-O(3)#2	49.1(3)
B(2)-O(5)#4	1.48(2)	O(3)-Ba/Pb-O(3)#2	146.4(3)
B(2)-O(6)	1.515(17)	O(7)-Ba/Pb-O(3)#2	65.3(3)
B(3)-O(3)#5	1.46(2)	O(8)#1-Ba/Pb-O(3)#2	116.1(3)
B(3)-O(4)#2	1.47(2)	O(5)-Ba/Pb-O(3)#2	61.3(3)
B(3)-O(7)	1.48(2)	O(2)-Ba/Pb-O(3)#2	118.2(3)
B(3)-O(8)#6	1.48(2)	O(8)-B(1)-O(5)	121.8(14)
B(4)-O(2)	1.368(12)	O(8)-B(1)-O(3)#3	120.0(14)
B(4)-O(2)#3	1.368(12)	O(5)-B(1)-O(3)#3	118.2(15)
B(4)-O(2)#7	1.368(12)	O(4)-B(2)-O(7)	107.8(12)
O(1)-Ba/Pb-O(4)	85.1(5)	O(4)-B(2)-O(5)#4	109.9(12)
O(1)-Ba/Pb-O(7)#1	98.7(4)	O(7)-B(2)-O(5)#4	112.9(13)

O(4)-Ba/Pb-O(7)#1	157.8(3)	O(4)-B(2)-O(6)	109.6(12)
O(1)-Ba/Pb-O(3)	75.2(2)	O(7)-B(2)-O(6)	108.8(11)
O(4)-Ba/Pb-O(3)	64.4(3)	O(5)#4-B(2)-O(6)	107.9(13)
O(7)#1-Ba/Pb-O(3)	137.8(3)	O(3)#5-B(3)-O(7)	109.6(13)
O(1)-Ba/Pb-O(7)	86.0(5)	O(4)#2-B(3)-O(7)	109.4(14)
O(4)-Ba/Pb-O(7)	51.3(3)	O(3)#5-B(3)-O(8)#6	106.5(14)
O(7)#1-Ba/Pb-O(7)	106.9(3)	O(4)#2-B(3)-O(8)#6	111.0(13)
O(3)-Ba/Pb-O(7)	114.2(3)	O(7)-B(3)-O(8)#6	110.5(14)
O(1)-Ba/Pb-O(8)#1	71.5(5)	O(2)-B(4)-O(2)#3	119.7(4)
O(4)-Ba/Pb-O(8)#1	112.9(3)	O(2)-B(4)-O(2)#7	119.7(4)
O(7)#1-Ba/Pb-O(8)#1	88.9(3)	O(2)#3-B(4)-O(2)#7	119.7(4)
O(3)-Ba/Pb-O(8)#1	49.2(3)		

Symmetry transformations used to generate equivalent atoms:

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

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

#7 -x+y+1,-x+2,z #8 -y+1,x-y+1,z

#9 -x+1,-x+y+1,z-1/2 #10 -x+y+1,-x+1,z

Table S2c. Selected bond lengths (Å) and angels (deg) for Compound **III**.

Pb(1)-O(7)	2.3934(17)	O(7)-Pb(1)-O(6)#2	94.9(2)
Pb(1)-O(2)#1	2.520(6)	O(2)#1-Pb(1)-O(6)#2	158.25(17)
Pb(1)-O(4)	2.696(5)	O(4)-Pb(1)-O(6)#2	136.17(17)
Pb(1)-O(6)#2	2.736(6)	O(5)-B(1)-O(2)	111.9(6)
B(1)-O(5)	1.449(10)	O(5)-B(1)-O(6)#3	111.5(6)
B(1)-O(2)	1.469(10)	O(2)-B(1)-O(6)#3	110.3(6)
B(1)-O(6)#3	1.474(10)	O(5)-B(1)-O(4)	105.9(6)
B(1)-O(4)	1.484(10)	O(2)-B(1)-O(4)	108.7(6)
B(2)-O(6)	1.443(9)	O(6)#3-B(1)-O(4)	108.4(6)
B(2)-O(2)	1.458(10)	O(6)-B(2)-O(2)	108.2(6)
B(2)-O(1)	1.477(10)	O(6)-B(2)-O(1)	112.0(6)
B(2)-O(3)	1.509(9)	O(2)-B(2)-O(1)	109.9(6)
B(3)-O(5)#1	1.357(10)	O(6)-B(2)-O(3)	110.3(6)
B(3)-O(4)	1.384(10)	O(2)-B(2)-O(3)	108.1(6)
B(3)-O(1)	1.388(10)	O(1)-B(2)-O(3)	108.2(7)
B(4)-O(8)#4	1.358(7)	O(5)#1-B(3)-O(4)	120.5(7)
B(4)-O(8)	1.358(7)	O(5)#1-B(3)-O(1)	119.1(7)
B(4)-O(8)#5	1.358(7)	O(4)-B(3)-O(1)	120.4(7)
O(7)-Pb(1)-O(2)#1	91.0(3)	O(8)#4-B(4)-O(8)	119.99(5)
O(7)-Pb(1)-O(4)	76.91(12)	O(8)#4-B(4)-O(8)#5	119.99(5)
O(2)#1-Pb(1)-O(4)	65.58(17)	O(8)-B(4)-O(8)#5	119.99(5)

Symmetry transformations used to generate equivalent atoms:

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

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

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

#9 -x+y+1,-x+1,z#10 -y+1,x-y,z

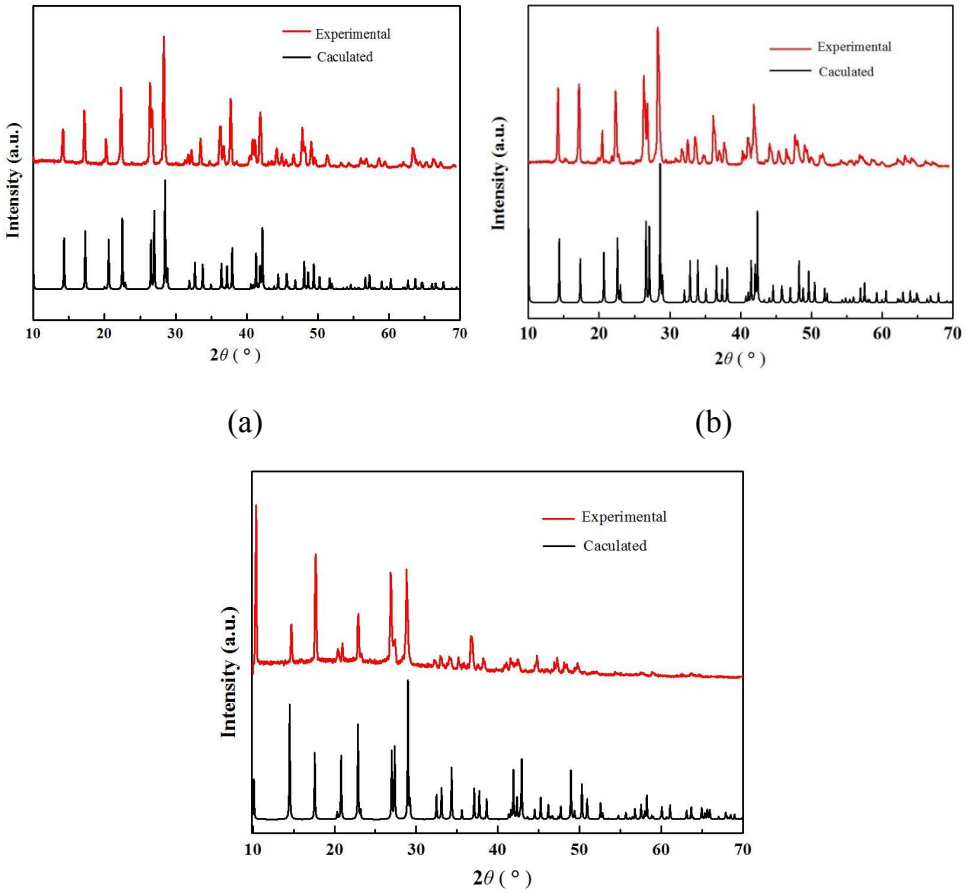
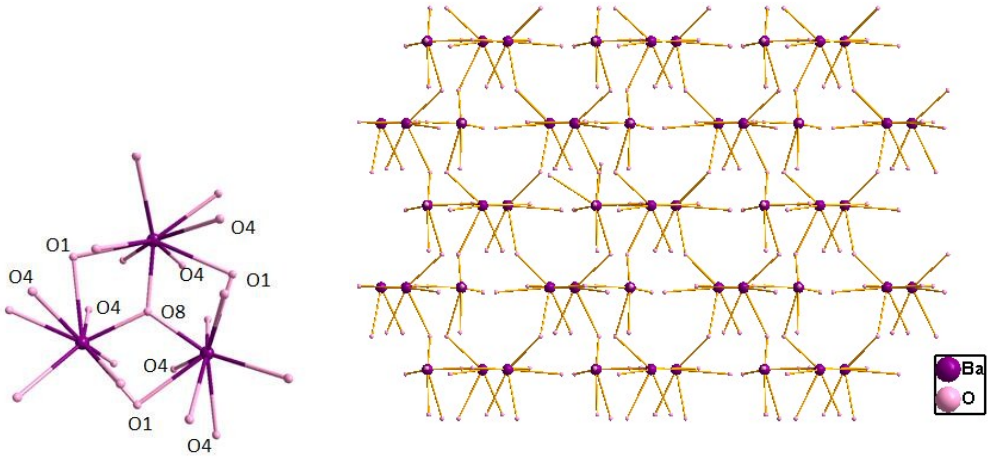
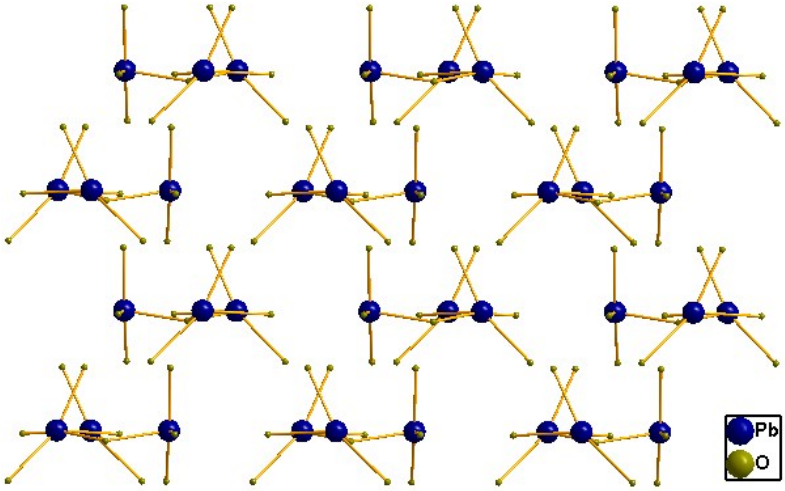


Figure S1. Experimental and calculated XRD patterns of compounds **I** (a), **II** (b) and **III** (c).



(a)



(b)

Figure S2. (a) The Ba/PbO_9 polyhedra connect with each other by sharing edge to form the Ba-O framework. (b) Three PbO_4 tetrahedra are linked by sharing O7 atoms to form the isolated Pb_3O_{10} trimer.

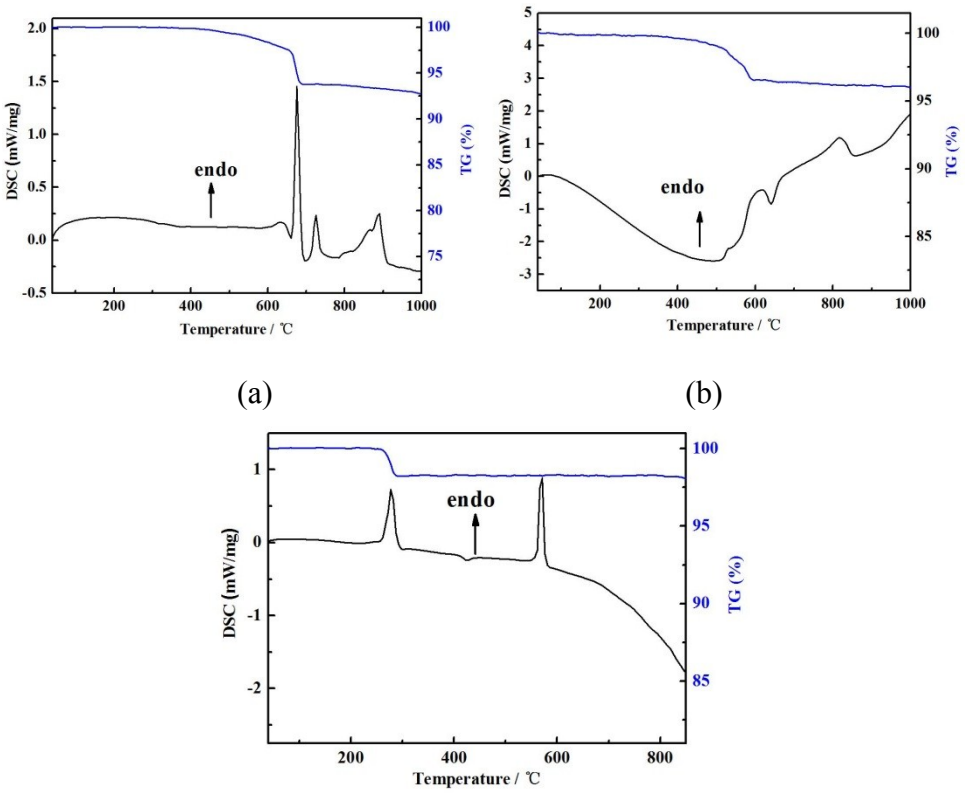


Figure S3. TG-DSC curves for compounds **I** (a), **II** (b) and **III** (c).

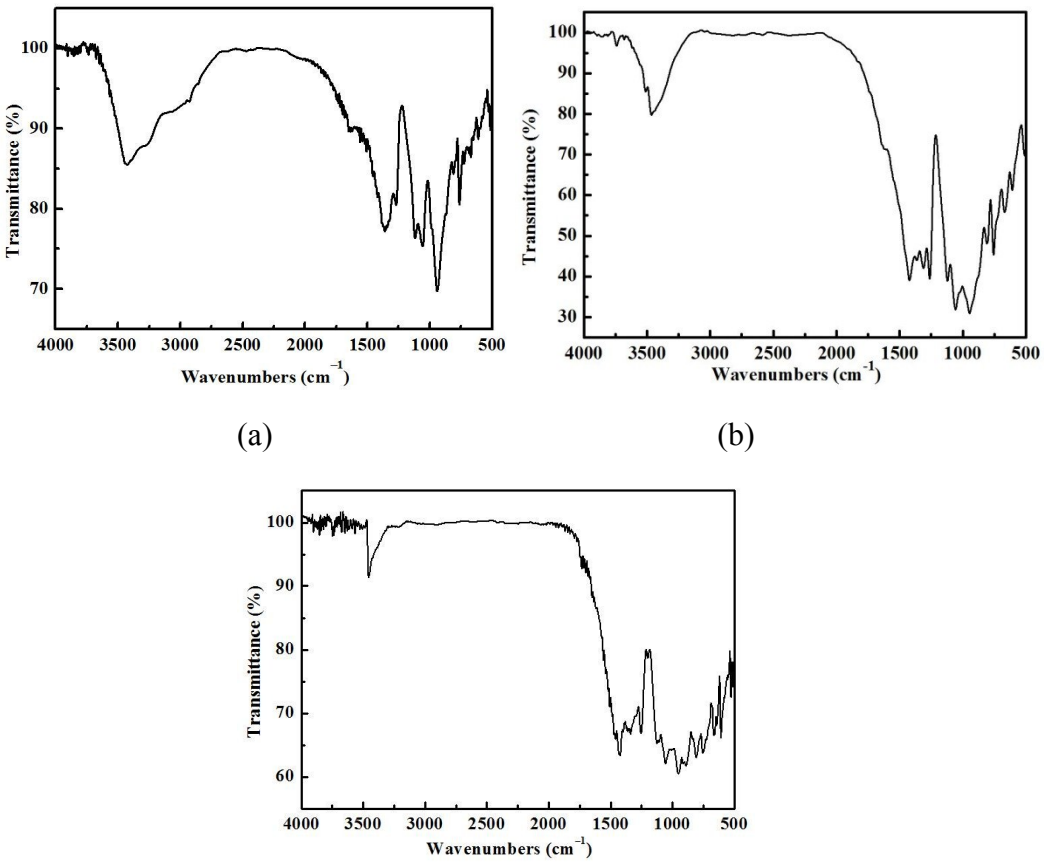


Figure S4. IR spectra for compounds **I** (a), **II** (b) and **III** (c).

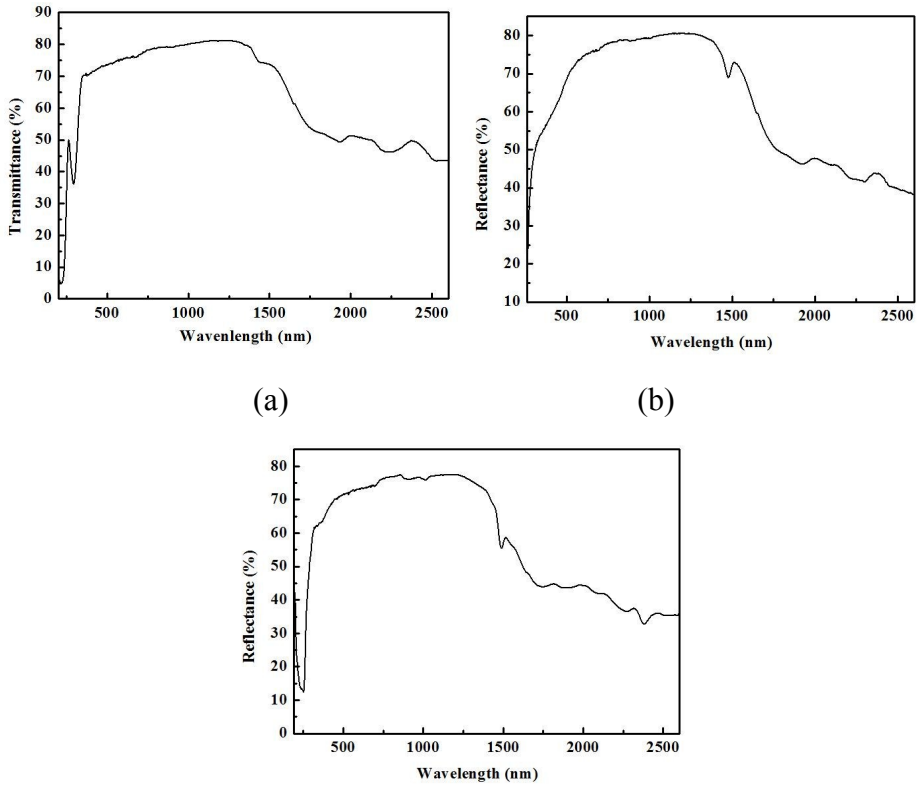


Figure S5. UV−VIS−NIR diffuse reflectance spectra for compounds **I** (a), **II** (b) and **III** (c).