Supporting Information

A Novel Deep UV Nonlinear Optical Crystal Ba$_3$B$_6$O$_{11}$F$_2$, with a New Fundamental Building

Block B$_6$O$_{14}$ Group

Honwei Yu,[a,b] Hongping Wu,[a] Shilie Pan,*[a] Zhihua Yang,[a] Xin Su[a] and Fangfang Zhang[a]

[a]*Xinjiang Key Laboratory of Electronic Information Materials and Devices, Xinjiang   Technical*

Institute of Physics & Chemistry, Chinese Academy of Sciences, 40-1 South Beijing Road, Urumqi

830011, China

[b]*Graduate school of Chinese Academy of Sciences, Beijing 100049, China*

*Corresponding author. E-mail: slpan@ms.xjb.ac.cn. Tel: (86)991-3674558. Fax:

(86)991-3838957

Table S1. Selected bond distances (Å) and angles (deg) for $Ba_3B_6O_{11}F_2$.

Ba(1)-F(2)	2.519(4)	B(1)-O(3)	1.489(7)
Ba(1)-F(1)#1	2.579(4)	B(1)-O(9)	1.527(7)
Ba(1)-O(10)	2.720(4)	B(2)-O(8)	1.361(6)
Ba(1)-O(3)	2.748(6)	B(2)-O(11)	1.362(7)
Ba(1)-O(4)	2.750(4)	B(2)-O(2)#11	1.373(6)
Ba(1)-O(7)#2	2.806(3)	B(3)-O(9)#12	1.357(8)
Ba(1)-O(2)#3	2.964(4)	B(3)-O(4)	1.370(7)
Ba(1)-O(11)	3.124(4)	B(3)-O(6)	1.380(7)
Ba(1)-O(5)#4	3.316(4)	B(4)-O(10)	1.455(6)
Ba(2)-F(1)	2.530(5)	B(4)-O(7)#2	1.475(7)
Ba(2)-F(1)#3	2.560(5)	B(4)-O(5)#11	1.478(6)
Ba(2)-O(2)	2.735(3)	B(4)-O(4)#10	1.523(6)
Ba(2)-O(1)	2.750(4)	B(5)-O(1)	1.442(8)
Ba(2)-O(9)#5	2.768(4)	B(5)-O(5)#9	1.443(7)
Ba(2)-O(8)	2.807(3)	B(5)-O(2)#6	1.507(7)
Ba(2)-O(11)#6	2.898(4)	B(5)-O(6)#8	1.514(6)
Ba(2)-O(6)#7	2.957(4)	B(6)-O(3)	1.434(7)
Ba(2)-O(3)#5	3.101(3)	B(6)-O(1)	1.444(7)
Ba(3)-F(2)	2.540(5)	B(6)-O(11)#7	1.518(7)
Ba(3)-F(2)#9	2.545(5)	B(6)-O(8)	1.529(7)
Ba(3)-O(5)	2.684(3)	F(2)-Ba(1)-F(1)#1	154.8(2)
Ba(3)-O(7)	2.718(3)	F(2)-Ba(1)-O(10)	84.89(13)
Ba(3)-O(9)#5	2.728(4)	F(1)#1-Ba(1)-O(10)	80.36(12)
Ba(3)-O(1)	2.807(4)	F(2)-Ba(1)-O(3)	79.40(13)
Ba(3)-O(5)#9	3.119(4)	F(1)#1-Ba(1)-O(3)	75.49(12)
Ba(3)-O(10)#5	3.139(3)	O(10)-Ba(1)-O(3)	50.27(10)
Ba(3)-O(6)#10	3.145(4)	F(2)-Ba(1)-O(4)	109.08(13)
Ba(3)-O(3)	3.297(3)	F(1)#1-Ba(1)-O(4)	95.18(13)
Ba(3)-O(4)#10	3.324(4)	O(10)-Ba(1)-O(4)	110.38(10)
B(1)-O(7)	1.447(7)	O(3)-Ba(1)-O(4)	159.19(9)
B(1)-O(10)	1.462(7)	F(2)-Ba(1)-O(7)#2	80.01(12)
F(1)#1-Ba(1)-O(7)#2	105.53(11)	F(1)#1-Ba(1)-O(5)#4	137.09(13)
O(10)-Ba(1)-O(7)#2	50.91(11)	O(10)-Ba(1)-O(5)#4	125.96(10)
O(3)-Ba(1)-O(7)#2	99.43(11)	O(3)-Ba(1)-O(5)#4	147.15(8)
O(4)-Ba(1)-O(7)#2	64.69(11)	O(4)-Ba(1)-O(5)#4	46.71(9)
F(2)-Ba(1)-O(2)#3	87.29(13)	O(7)#2-Ba(1)-O(5)#4	78.10(9)
F(1)#1-Ba(1)-O(2)#3	109.21(12)	O(2)#3-Ba(1)-O(5)#4	44.41(9)
O(10)-Ba(1)-O(2)#3	169.80(11)	O(11)-Ba(1)-O(5)#4	101.36(9)
O(3)-Ba(1)-O(2)#3	134.29(9)	F(1)-Ba(2)-F(1)#3	153.11(12)
O(4)-Ba(1)-O(2)#3	66.17(10)	F(1)-Ba(2)-O(2)	102.25(13)
O(7)#2-Ba(1)-O(2)#3	121.14(11)	F(1)#3-Ba(2)-O(2)	73.83(13)
F(2)-Ba(1)-O(11)	100.06(11)	F(1)-Ba(2)-O(1)	75.67(13)
F(1)#1-Ba(1)-O(11)	74.67(11)	F(1)#3-Ba(2)-O(1)	107.81(13)

O(10)-Ba(1)-O(11)	129.69(12)	O(2)-Ba(2)-O(1)	177.87(12)
O(3)-Ba(1)-O(11)	81.17(10)	F(1)-Ba(2)-O(9)#5	112.40(14)
O(4)-Ba(1)-O(11)	114.74(11)	F(1)#3-Ba(2)-O(9)#5	91.53(13)
O(7)#2-Ba(1)-O(11)	179.40(12)	O(2)-Ba(2)-O(9)#5	120.36(10)
O(2)#3-Ba(1)-O(11)	58.28(10)	O(1)-Ba(2)-O(9)#5	61.22(13)
F(2)-Ba(1)-O(5)#4	67.86(14)	F(1)-Ba(2)-O(8)	76.82(13)
F(1)#3-Ba(2)-O(8)	85.21(12)	O(7)-Ba(3)-O(1)	70.89(11)
O(2)-Ba(2)-O(8)	129.09(11)	O(9)#5-Ba(3)-O(1)	60.99(13)
O(1)-Ba(2)-O(8)	50.24(11)	F(2)-Ba(3)-O(5)#9	137.07(11)
O(9)#5-Ba(2)-O(8)	105.74(11)	F(2)#9-Ba(3)-O(5)#9	68.22(12)
F(1)-Ba(2)-O(11)#6	89.75(12)	O(5)-Ba(3)-O(5)#9	146.94(11)
F(1)#3-Ba(2)-O(11)#6	110.85(12)	O(7)-Ba(3)-O(5)#9	49.13(9)
O(2)-Ba(2)-O(11)#6	63.50(10)	O(9)#5-Ba(3)-O(5)#9	76.65(11)
O(1)-Ba(2)-O(11)#6	116.69(12)	O(1)-Ba(3)-O(5)#9	48.19(11)
O(9)#5-Ba(2)-O(11)#6	69.55(11)	F(2)-Ba(3)-O(10)#5	78.54(12)
O(8)-Ba(2)-O(11)#6	163.02(13)	F(2)#9-Ba(3)-O(10)#5	84.44(12)
F(1)-Ba(2)-O(6)#7	78.71(14)	O(5)-Ba(3)-O(10)#5	46.73(9)
F(1)#3-Ba(2)-O(6)#7	78.91(13)	O(7)-Ba(3)-O(10)#5	171.56(11)
O(2)-Ba(2)-O(6)#7	49.76(9)	O(9)#5-Ba(3)-O(10)#5	48.14(11)
O(1)-Ba(2)-O(6)#7	128.89(10)	O(1)-Ba(3)-O(10)#5	100.98(10)
O(9)#5-Ba(2)-O(6)#7	167.76(11)	O(5)#9-Ba(3)-O(10)#5	123.79(10)
O(8)-Ba(2)-O(6)#7	81.27(10)	F(2)-Ba(3)-O(6)#10	81.04(13)
O(11)#6-Ba(2)-O(6)#7	106.54(10)	F(2)#9-Ba(3)-O(6)#10	81.56(13)
F(1)-Ba(2)-O(3)#5	135.64(14)	O(5)-Ba(3)-O(6)#10	47.15(9)
F(1)#3-Ba(2)-O(3)#5	69.67(14)	O(7)-Ba(3)-O(6)#10	94.48(10)
O(2)-Ba(2)-O(3)#5	73.13(9)	O(9)#5-Ba(3)-O(6)#10	135.30(10)
O(1)-Ba(2)-O(3)#5	108.65(10)	O(1)-Ba(3)-O(6)#10	163.68(9)
O(9)#5-Ba(2)-O(3)#5	48.01(10)	O(5)#9-Ba(3)-O(6)#10	126.84(10)
O(8)-Ba(2)-O(3)#5	140.78(11)	O(10)#5-Ba(3)-O(6)#10	93.87(9)
O(11)#6-Ba(2)-O(3)#5	47.89(11)	F(2)-Ba(3)-O(3)	69.11(14)
O(6)#7-Ba(2)-O(3)#5	120.53(10)	F(2)#9-Ba(3)-O(3)	135.94(14)
F(2)-Ba(3)-F(2)#9	154.68(12)	O(5)-Ba(3)-O(3)	144.35(14)
F(2)-Ba(3)-O(5)	75.81(13)	O(7)-Ba(3)-O(3)	47.74(10)
F(2)#9-Ba(3)-O(5)	78.87(14)	O(9)#5-Ba(3)-O(3)	104.80(10)
F(2)-Ba(3)-O(7)	104.01(12)	O(1)-Ba(3)-O(3)	45.84(10)
F(2)#9-Ba(3)-O(7)	95.56(12)	O(5)#9-Ba(3)-O(3)	68.63(11)
O(5)-Ba(3)-O(7)	141.57(10)	O(10)#5-Ba(3)-O(3)	128.00(10)
F(2)-Ba(3)-O(9)#5	107.44(13)	O(6)#10-Ba(3)-O(3)	118.79(9)
F(2)#9-Ba(3)-O(9)#5	73.31(13)	F(2)-Ba(3)-O(4)#10	72.85(12)
O(5)-Ba(3)-O(9)#5	91.34(11)	F(2)#9-Ba(3)-O(4)#10	105.48(12)
O(7)-Ba(3)-O(9)#5	123.78(12)	O(5)-Ba(3)-O(4)#10	86.66(9)
F(2)-Ba(3)-O(1)	95.23(13)	O(7)-Ba(3)-O(4)#10	57.91(10)
F(2)#9-Ba(3)-O(1)	106.40(13)	O(9)#5-Ba(3)-O(4)#10	177.85(11)
O(5)-Ba(3)-O(1)	147.35(10)	O(1)-Ba(3)-O(4)#10	121.16(9)

O(5)#9-Ba(3)-O(4)#10	104.64(9)	O(10)-B(4)-O(5)#11	106.3(4)
O(10)#5-Ba(3)-O(4)#10	130.24(11)	O(7)#2-B(4)-O(5)#11	112.4(4)
O(6)#10-Ba(3)-O(4)#10	42.54(8)	O(10)-B(4)-O(4)#10	110.9(4)
O(3)-Ba(3)-O(4)#10	77.32(8)	O(7)#2-B(4)-O(4)#10	108.6(4)
B(3)#10-Ba(3)-O(4)#10	23.84(11)	O(5)#11-B(4)-O(4)#10	110.1(4)
O(7)-B(1)-O(10)	113.6(5)	O(1)-B(5)-O(5)#9	115.2(5)
O(7)-B(1)-O(3)	116.1(4)	O(1)-B(5)-O(2)#6	110.6(4)
O(10)-B(1)-O(3)	103.8(4)	O(5)#9-B(5)-O(2)#6	108.5(4)
O(7)-B(1)-O(9)	108.7(5)	O(1)-B(5)-O(6)#8	110.1(4)
O(10)-B(1)-O(9)	108.3(4)	O(5)#9-B(5)-O(6)#8	106.5(4)
O(3)-B(1)-O(9)	105.9(4)	O(2)#6-B(5)-O(6)#8	105.4(4)
O(8)-B(2)-O(11)	120.0(4)	O(3)-B(6)-O(1)	114.5(5)
O(8)-B(2)-O(2)#11	118.6(5)	O(3)-B(6)-O(11)#7	111.6(4)
O(11)-B(2)-O(2)#11	121.5(4)	O(1)-B(6)-O(11)#7	110.8(5)
O(9)#12-B(3)-O(4)	121.7(5)	O(3)-B(6)-O(8)	106.3(5)
O(9)#12-B(3)-O(6)	120.6(5)	O(1)-B(6)-O(8)	105.1(4)
O(4)-B(3)-O(6)	117.7(5)	O(11)#7-B(6)-O(8)	108.1(4)
O(10)-B(4)-O(7)#2	108.5(4)		

Note. Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y+1/2,-z+2; #2 -x+1,y+1/2,-z+1; #3 -x,y+1/2,-z+2; #4 -x,y+1/2,-z+1; #5 x-1,y,z;
#6 -x,y-1/2,-z+2; #7 -x+1,y-1/2,-z+2; #8 x-1,y-1,z; #9 -x,y-1/2,-z+1; #10 -x+1,y-1/2,-z+1;
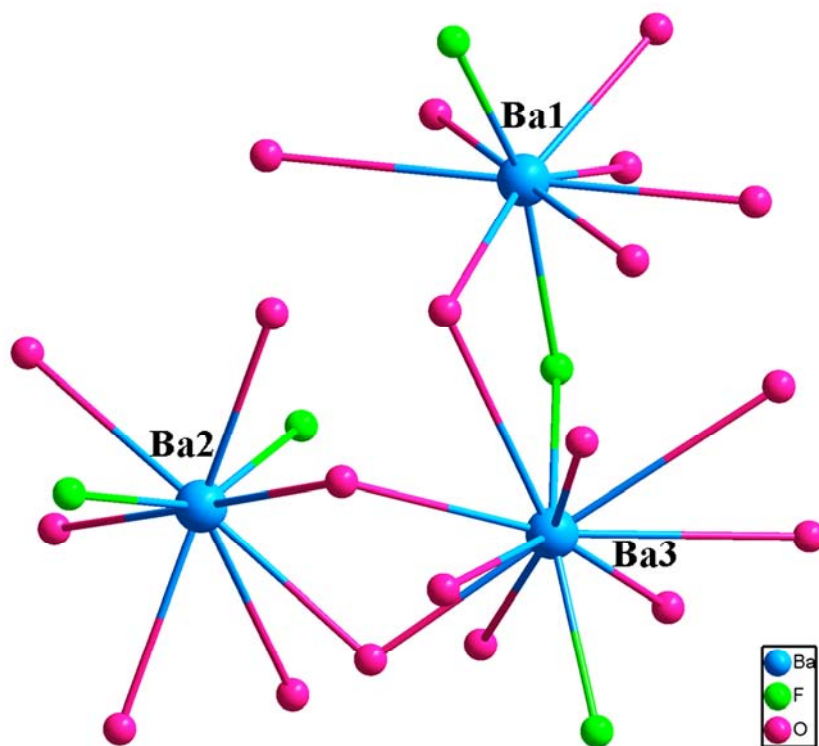
#11 x+1,y,z; #12 x,y+1,z; #13 x+1,y+1,z; #14 x,y-1,z

Figure S1. Barium-coordinated environments.

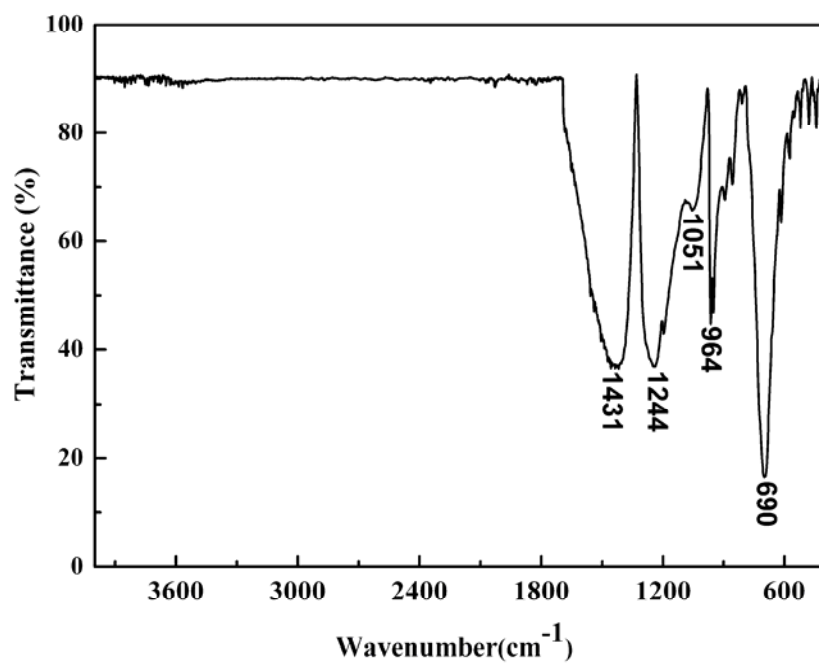**Figure S2.** The IR spectrum of $Ba_3B_6O_{11}F_2$.