## **Supporting Information**

A Novel Deep UV Nonlinear Optical Crystal Ba<sub>3</sub>B<sub>6</sub>O<sub>11</sub>F<sub>2</sub>, with a New Fundamental Building

## Block B<sub>6</sub>O<sub>14</sub> Group

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Table 51. Selected bolle	i distances (11) di	In all gives ( $(UCg)$ ) for $Du_3D_6O$	111 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)

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$\begin{array}{llllllllllllllllllllllllllllllllllll$	)-Ba(1)-O(11)	129.69(12)	O(2)-Ba(2)-O(1)	177.87(12)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	-Ba(1)-O(11) 8	81.17(10)	F(1)-Ba(2)-O(9)#5	112.40(14)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-Ba(1)-O(11)	114.74(11)	F(1)#3-Ba(2)-O(9)#5	91.53(13)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	#2-Ba(1)-O(11)	179.40(12)	O(2)-Ba(2)-O(9)#5	120.36(10)
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(5)#9 $137.07(11)$ $O(9)$ #5-Ba(2)-O(8) $105.74(11)$ $F(2)$ -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 $48.19(11)$ $O(2)$ -Ba(2)-O(11)#6 $110.85(12)$ $O(7)$ -Ba(3)-O(5)#9 $48.19(11)$ $O(2)$ -Ba(2)-O(11)#6 $61.50(12)$ $O(1)$ -Ba(3)-O(5)#9 $48.19(11)$ $O(2)$ -Ba(2)-O(11)#6 $69.55(11)$ $F(2)$ -Ba(3)-O(10)#5 $78.54(12)$ $O(3)$ -Ba(2)-O(1)#6 $69.55(11)$ $F(2)$ -Ba(3)-O(10)#5 $84.44(12)$ $F(1)$ -Ba(2)-O(1)#6 $69.55(11)$ $F(2)$ -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 $45.73(9)$ $F(1)$ +Ba(2)-O(6)#7 $78.71(14)$ $O(5)$ -Ba(3)-O(10)#5 $48.14(11)$ $O(2)$ -Ba(2)-O(6)#7 $78.71(14)$ $O(5)$ -Ba(3)-O(10)#5 $48.14(11)$ $O(1)$ -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 $18.27(10)$ $F(2)$ -Ba(3)-O(6)#10 $81.56(13)$ $F(1)$ -Ba(2)-O(6)#7 $18.27(10)$ $F(2)$ -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 $81.56(13)$ $O(1)$ +Ba(2)-O(3)#5 $135.64(14)$ $O(5)$ -Ba(3)-O(6)#10 $81.56(13)$ $O(1)$ +Ba(2)-O(3)#5 $135.64(14)$ $O(5)$ -Ba(3)-O(6)#10 $81.56(13)$ $F(1)$ -Ba(2)	#3-Ba(1)-O(11) 5	58.28(10)	O(1)-Ba(2)-O(9)#5	61.22(13)
F(1)#3-Ba(2)-O(8) $85.21(12)$ $O(7)-Ba(3)-O(1)$ $70.89(11)$ $O(2)-Ba(2)-O(8)$ $129.09(11)$ $O(9)#5-Ba(3)-O(5)#9$ $137.07(11)$ $O(9)#5-Ba(2)-O(8)$ $105.74(11)$ $F(2)-Ba(3)-O(5)#9$ $137.07(11)$ $O(9)#5-Ba(2)-O(11)#6$ $89.75(12)$ $O(5)-Ba(3)-O(5)#9$ $46.94(11)$ $F(1)+Ba(2)-O(11)#6$ $110.85(12)$ $O(7)-Ba(3)-O(5)#9$ $46.94(11)$ $F(1)+Ba(2)-O(11)#6$ $110.85(12)$ $O(7)-Ba(3)-O(5)#9$ $48.19(11)$ $O(2)-Ba(2)-O(11)#6$ $63.50(10)$ $O(9)#5-Ba(3)-O(5)#9$ $48.19(11)$ $O(9)#5-Ba(2)-O(11)#6$ $163.02(13)$ $F(2)#9-Ba(3)-O(10)#5$ $84.44(12)$ $F(1)-Ba(2)-O(6)#7$ $78.71(14)$ $O(5)-Ba(3)-O(10)#5$ $84.44(12)$ $F(1)-Ba(2)-O(6)#7$ $78.71(14)$ $O(5)-Ba(3)-O(10)#5$ $46.73(9)$ $F(1)#3-Ba(2)-O(6)#7$ $78.91(13)$ $O(7)-Ba(3)-O(10)#5$ $40.73(9)$ $F(1)#3-Ba(2)-O(6)#7$ $78.91(13)$ $O(7)-Ba(3)-O(10)#5$ $40.73(9)$ $F(1)=Ba(2)-O(6)#7$ $78.71(14)$ $O(5)-Ba(3)-O(10)#5$ $40.73(9)$ $O(9)#5-Ba(2)-O(6)#7$ $167.76(11)$ $O(5)=Ba(3)-O(10)#5$ $100.81(10)$ $O(9)=5-Ba(2)-O(6)#7$ $167.76(11)$ $O(5)=Ba(3)-O(6)#10$ $81.04(13)$ $O(1)=Ba(2)-O(6)#7$ $1167.76(11)$ $O(5)=Ba(3)-O(6)#10$ $81.56(13)$ $F(1)=Ba(2)-O(3)#5$ $135.64(14)$ $O(7)-Ba(3)-O(6)#10$ $81.56(13)$ $F(1)=Ba(2)-O(3)#5$ $135.64(14)$ $O(7)-Ba(3)-O(6)#10$ $14.56(13)$ $O(1)=Ba(2)-O(3)#5$ $140.78(11)$ $O(1)=Ba(3)-O(6)#10$ $135.94(14)$ <td>Ba(1)-O(5)#4 6</td> <td>67.86(14)</td> <td>F(1)-Ba(2)-O(8)</td> <td>76.82(13)</td>	Ba(1)-O(5)#4 6	67.86(14)	F(1)-Ba(2)-O(8)	76.82(13)
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$\begin{array}{llllllllllllllllllllllllllllllllllll$	#5-Ba(2)-O(8)	105.74(11)	F(2)#9-Ba(3)-O(5)#9	68.22(12)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Ba(2)-O(11)#6 8	89.75(12)	O(5)-Ba(3)-O(5)#9	146.94(11)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	<sup>4</sup> 3-Ba(2)-O(11)#6	110.85(12)	O(7)-Ba(3)-O(5)#9	49.13(9)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	-Ba(2)-O(11)#6 6	63.50(10)	O(9)#5-Ba(3)-O(5)#9	76.65(11)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	-Ba(2)-O(11)#6	116.69(12)	O(1)-Ba(3)-O(5)#9	48.19(11)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	#5-Ba(2)-O(11)#6 6	69.55(11)	F(2)-Ba(3)-O(10)#5	78.54(12)
F(1)-Ba(2)-O(6)#7 $78.71(14)$ $O(5)-Ba(3)-O(10)#5$ $46.73(9)$ $F(1)#3-Ba(2)-O(6)#7$ $78.91(13)$ $O(7)-Ba(3)-O(10)#5$ $171.56(11)$ $O(2)-Ba(2)-O(6)#7$ $49.76(9)$ $O(9)#5-Ba(3)-O(10)#5$ $48.14(11)$ $O(1)-Ba(2)-O(6)#7$ $128.89(10)$ $O(1)-Ba(3)-O(10)#5$ $100.98(10)$ $O(9)#5-Ba(2)-O(6)#7$ $167.76(11)$ $O(5)#9-Ba(3)-O(10)#5$ $123.79(10)$ $O(8)-Ba(2)-O(6)#7$ $81.27(10)$ $F(2)-Ba(3)-O(6)#10$ $81.04(13)$ $O(11)#6-Ba(2)-O(6)#7$ $106.54(10)$ $F(2)#9-Ba(3)-O(6)#10$ $81.56(13)$ $F(1)-Ba(2)-O(3)#5$ $135.64(14)$ $O(5)-Ba(3)-O(6)#10$ $47.15(9)$ $F(1)#3-Ba(2)-O(3)#5$ $69.67(14)$ $O(7)-Ba(3)-O(6)#10$ $135.30(10)$ $O(2)-Ba(2)-O(3)#5$ $73.13(9)$ $O(9)#5-Ba(3)-O(6)#10$ $135.30(10)$ $O(1)-Ba(2)-O(3)#5$ $108.65(10)$ $O(1)-Ba(3)-O(6)#10$ $163.68(9)$ $O(9)#5-Ba(2)-O(3)#5$ $108.65(10)$ $O(1)-Ba(3)-O(6)#10$ $126.84(10)$ $O(8)-Ba(2)-O(3)#5$ $140.78(11)$ $O(10)#5-Ba(3)-O(6)#10$ $126.84(10)$ $O(8)-Ba(2)-O(3)#5$ $140.78(11)$ $O(10)#5-Ba(3)-O(3)$ $135.94(14)$ $F(2)-Ba(3)-O(5)$ $75.81(13)$ $O(7)-Ba(3)-O(3)$ $144.35(14)$ $F(2)-Ba(3)-O(5)$ $78.87(14)$ $O(9)#5-Ba(3)-O(3)$ $144.35(14)$ $F(2)-Ba(3)-O(7)$ $154.68(12)$ $O(5)-Ba(3)-O(3)$ $45.84(10)$ $F(2)-Ba(3)-O(7)$ $154.68(12)$ $O(5)-Ba(3)-O(3)$ $45.84(10)$ $F(2)-Ba(3)-O(7)$ $154.68(12)$ $O(5)-Ba(3)-O(3)$ $45.84(10)$ <td< td=""><td>-Ba(2)-O(11)#6</td><td>163.02(13)</td><td>F(2)#9-Ba(3)-O(10)#5</td><td>84.44(12)</td></td<>	-Ba(2)-O(11)#6	163.02(13)	F(2)#9-Ba(3)-O(10)#5	84.44(12)
F(1)#3-Ba(2)-O(6)#7 $78.91(13)$ $O(7)-Ba(3)-O(10)#5$ $171.56(11)$ $O(2)-Ba(2)-O(6)#7$ $49.76(9)$ $O(9)#5-Ba(3)-O(10)#5$ $48.14(11)$ $O(1)-Ba(2)-O(6)#7$ $128.89(10)$ $O(1)-Ba(3)-O(10)#5$ $100.98(10)$ $O(9)#5-Ba(2)-O(6)#7$ $167.76(11)$ $O(5)#9-Ba(3)-O(10)#5$ $123.79(10)$ $O(8)-Ba(2)-O(6)#7$ $81.27(10)$ $F(2)-Ba(3)-O(6)#10$ $81.04(13)$ $O(11)#6-Ba(2)-O(6)#7$ $81.27(10)$ $F(2)#9-Ba(3)-O(6)#10$ $81.56(13)$ $F(1)-Ba(2)-O(3)#5$ $135.64(14)$ $O(5)-Ba(3)-O(6)#10$ $47.15(9)$ $F(1)#3-Ba(2)-O(3)#5$ $69.67(14)$ $O(7)-Ba(3)-O(6)#10$ $135.30(10)$ $O(2)-Ba(2)-O(3)#5$ $73.13(9)$ $O(9)#5-Ba(3)-O(6)#10$ $135.30(10)$ $O(1)-Ba(2)-O(3)#5$ $108.65(10)$ $O(1)-Ba(3)-O(6)#10$ $163.68(9)$ $O(9)#5-Ba(2)-O(3)#5$ $140.78(11)$ $O(10)#5-Ba(3)-O(6)#10$ $126.84(10)$ $O(8)-Ba(2)-O(3)#5$ $140.78(11)$ $O(10)#5-Ba(3)-O(6)#10$ $126.84(10)$ $O(8)-Ba(2)-O(3)#5$ $140.78(11)$ $O(10)#5-Ba(3)-O(6)#10$ $135.30(10)$ $O(11)#6-Ba(2)-O(3)#5$ $120.53(10)$ $F(2)#9-Ba(3)-O(3)$ $134.35(14)$ $F(2)-Ba(3)-O(5)$ $75.81(13)$ $O(7)-Ba(3)-O(3)$ $144.35(14)$ $F(2)-Ba(3)-O(5)$ $78.87(14)$ $O(9)#5-Ba(3)-O(3)$ $45.84(10)$ $F(2)#9-Ba(3)-O(7)$ $104.01(12)$ $O(1)-Ba(3)-O(3)$ $45.84(10)$ $F(2)=Ba(3)-O(7)$ $104.01(12)$ $O(5)#9-Ba(3)-O(3)$ $45.84(10)$ $F(2)=Ba(3)-O(7)$ $15.56(12)$ $O(5)#9-Ba(3)-O(3)$ $45.84(10)$ <td>Ba(2)-O(6)#7 7</td> <td>78.71(14)</td> <td>O(5)-Ba(3)-O(10)#5</td> <td>46.73(9)</td>	Ba(2)-O(6)#7 7	78.71(14)	O(5)-Ba(3)-O(10)#5	46.73(9)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	<sup>±</sup> 3-Ba(2)-O(6)#7 7	78.91(13)	O(7)-Ba(3)-O(10)#5	171.56(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-Ba(2)-O(6)#7 4	49.76(9)	O(9)#5-Ba(3)-O(10)#5	48.14(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-Ba(2)-O(6)#7	128.89(10)	O(1)-Ba(3)-O(10)#5	100.98(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	#5-Ba(2)-O(6)#7	167.76(11)	O(5)#9-Ba(3)-O(10)#5	123.79(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	·Ba(2)-O(6)#7 8	81.27(10)	F(2)-Ba(3)-O(6)#10	81.04(13)
$F(1)$ - $Ba(2)$ - $O(3)$ #5135.64(14) $O(5)$ - $Ba(3)$ - $O(6)$ #1047.15(9) $F(1)$ #3- $Ba(2)$ - $O(3)$ #569.67(14) $O(7)$ - $Ba(3)$ - $O(6)$ #1094.48(10) $O(2)$ - $Ba(2)$ - $O(3)$ #573.13(9) $O(9)$ #5- $Ba(3)$ - $O(6)$ #10135.30(10) $O(1)$ - $Ba(2)$ - $O(3)$ #5108.65(10) $O(1)$ - $Ba(3)$ - $O(6)$ #10163.68(9) $O(9)$ #5- $Ba(2)$ - $O(3)$ #5108.65(10) $O(1)$ - $Ba(3)$ - $O(6)$ #10126.84(10) $O(8)$ - $Ba(2)$ - $O(3)$ #5140.78(11) $O(10)$ #5- $Ba(3)$ - $O(6)$ #10126.84(10) $O(8)$ - $Ba(2)$ - $O(3)$ #5140.78(11) $O(10)$ #5- $Ba(3)$ - $O(6)$ #1093.87(9) $O(11)$ #6- $Ba(2)$ - $O(3)$ #547.89(11) $F(2)$ - $Ba(3)$ - $O(6)$ #1093.87(9) $O(11)$ #6- $Ba(2)$ - $O(3)$ #5120.53(10) $F(2)$ #9- $Ba(3)$ - $O(3)$ 69.11(14) $O(6)$ #7- $Ba(2)$ - $O(3)$ #5120.53(10) $F(2)$ #9- $Ba(3)$ - $O(3)$ 135.94(14) $F(2)$ - $Ba(3)$ - $O(5)$ 75.81(13) $O(7)$ - $Ba(3)$ - $O(3)$ 144.35(14) $F(2)$ - $Ba(3)$ - $O(5)$ 78.87(14) $O(9)$ #5- $Ba(3)$ - $O(3)$ 104.80(10) $F(2)$ #9- $Ba(3)$ - $O(7)$ 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- $Ba(3)$ - $O(3)$ 128.00(10) $F(2)$ = $Ba(3)$ - $O(7)$ 141.57(10) $O(10)$ #5- $Ba(3)$ - $O(3)$ 128.00(10) $F(2)$ - $Ba(3)$ - $O(9)$ #5107.44(13) $O(6)$ #10- $Ba(3)$ - $O(3)$ 118.79(9) $F(2)$ #9- $Ba(3)$ - $O(9)$ #573.31(13) $F(2)$ - $Ba(3)$ - $O(4)$ #1072.85(12) $O(5)$ $P_1$ $O(1)$ $P_2$ $P_2$ $P_3$ $O(1)$ $P_3$ $P_3$	)#6-Ba(2)-O(6)#7	106.54(10)	F(2)#9-Ba(3)-O(6)#10	81.56(13)
F(1)#3-Ba(2)-O(3)#5 $69.67(14)$ $O(7)-Ba(3)-O(6)#10$ $94.48(10)$ $O(2)-Ba(2)-O(3)#5$ $73.13(9)$ $O(9)#5-Ba(3)-O(6)#10$ $135.30(10)$ $O(1)-Ba(2)-O(3)#5$ $108.65(10)$ $O(1)-Ba(3)-O(6)#10$ $163.68(9)$ $O(9)#5-Ba(2)-O(3)#5$ $48.01(10)$ $O(5)#9-Ba(3)-O(6)#10$ $126.84(10)$ $O(8)-Ba(2)-O(3)#5$ $140.78(11)$ $O(10)#5-Ba(3)-O(6)#10$ $126.84(10)$ $O(8)-Ba(2)-O(3)#5$ $140.78(11)$ $O(10)#5-Ba(3)-O(6)#10$ $93.87(9)$ $O(11)#6-Ba(2)-O(3)#5$ $140.78(11)$ $O(10)#5-Ba(3)-O(6)#10$ $93.87(9)$ $O(11)#6-Ba(2)-O(3)#5$ $120.53(10)$ $F(2)+Ba(3)-O(3)$ $69.11(14)$ $O(6)#7-Ba(2)-O(3)#5$ $120.53(10)$ $F(2)#9-Ba(3)-O(3)$ $134.35(14)$ $F(2)-Ba(3)-F(2)#9$ $154.68(12)$ $O(5)-Ba(3)-O(3)$ $144.35(14)$ $F(2)-Ba(3)-O(5)$ $75.81(13)$ $O(7)-Ba(3)-O(3)$ $144.35(14)$ $F(2)-Ba(3)-O(5)$ $78.87(14)$ $O(9)#5-Ba(3)-O(3)$ $104.80(10)$ $F(2)+Ba(3)-O(5)$ $78.87(14)$ $O(9)#5-Ba(3)-O(3)$ $104.80(10)$ $F(2)+Ba(3)-O(7)$ $104.01(12)$ $O(1)-Ba(3)-O(3)$ $45.84(10)$ $F(2)+Ba(3)-O(7)$ $95.56(12)$ $O(5)#9-Ba(3)-O(3)$ $128.00(10)$ $F(2)-Ba(3)-O(7)$ $141.57(10)$ $O(10)#5-Ba(3)-O(3)$ $128.00(10)$ $F(2)-Ba(3)-O(9)#5$ $107.44(13)$ $O(6)#10-Ba(3)-O(3)$ $118.79(9)$ $F(2)#9-Ba(3)-O(9)#5$ $73.31(13)$ $F(2)-Ba(3)-O(4)#10$ $72.85(12)$ $O(5) = F(2)=O(2)#5$ $O(2) = 0(2)#5$ $O(2) = 0(2)#5$ $O(2) = 0(2)#5$ <td>Ba(2)-O(3)#5</td> <td>135.64(14)</td> <td>O(5)-Ba(3)-O(6)#10</td> <td>47.15(9)</td>	Ba(2)-O(3)#5	135.64(14)	O(5)-Ba(3)-O(6)#10	47.15(9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<sup>±</sup> 3-Ba(2)-O(3)#5	69.67(14)	O(7)-Ba(3)-O(6)#10	94.48(10)
O(1)-Ba(2)-O(3)#5108.65(10) $O(1)$ -Ba(3)-O(6)#10163.68(9) $O(9)$ #5-Ba(2)-O(3)#548.01(10) $O(5)$ #9-Ba(3)-O(6)#10126.84(10) $O(8)$ -Ba(2)-O(3)#5140.78(11) $O(10)$ #5-Ba(3)-O(6)#1093.87(9) $O(11)$ #6-Ba(2)-O(3)#547.89(11) $F(2)$ -Ba(3)-O(6)#1093.87(9) $O(1)$ #6-Ba(2)-O(3)#5120.53(10) $F(2)$ #9-Ba(3)-O(3)69.11(14) $O(6)$ #7-Ba(2)-O(3)#5120.53(10) $F(2)$ #9-Ba(3)-O(3)135.94(14) $F(2)$ -Ba(3)-F(2)#9154.68(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)#5107.44(13) $O(6)$ #10-Ba(3)-O(3)118.79(9) $F(2)$ #9-Ba(3)-O(9)#573.31(13) $F(2)$ -Ba(3)-O(4)#1072.85(12) $O(5)$ P $O(2)$ /15 $O(2)$ /16 $O(2)$ /16 $O(2)$ /16	·Ba(2)-O(3)#5	73.13(9)	O(9)#5-Ba(3)-O(6)#10	135.30(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-Ba(2)-O(3)#5 1	108.65(10)	O(1)-Ba(3)-O(6)#10	163.68(9)
O(8)-Ba(2)-O(3)#5140.78(11) $O(10)$ #5-Ba(3)-O(6)#1093.87(9) $O(11)$ #6-Ba(2)-O(3)#547.89(11) $F(2)$ -Ba(3)-O(3)69.11(14) $O(6)$ #7-Ba(2)-O(3)#5120.53(10) $F(2)$ #9-Ba(3)-O(3)135.94(14) $F(2)$ -Ba(3)- $F(2)$ #9154.68(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)- $O(9)$ #5107.44(13) $O(6)$ #10-Ba(3)- $O(3)$ 118.79(9) $F(2)$ #9-Ba(3)- $O(9)$ #573.31(13) $F(2)$ -Ba(3)- $O(4)$ #1072.85(12) $O(5)$ -Ba(3)- $O(9)$ #573.31(13) $F(2)$ -Ba(3)- $O(4)$ #1072.85(12)	#5-Ba(2)-O(3)#5 4	48.01(10)	O(5)#9-Ba(3)-O(6)#10	126.84(10)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-Ba(2)-O(3)#5 1	140.78(11)	O(10)#5-Ba(3)-O(6)#10	93.87(9)
O(6)#7-Ba(2)-O(3)#5 $120.53(10)$ $F(2)#9-Ba(3)-O(3)$ $135.94(14)$ $F(2)-Ba(3)-F(2)#9$ $154.68(12)$ $O(5)-Ba(3)-O(3)$ $144.35(14)$ $F(2)-Ba(3)-O(5)$ $75.81(13)$ $O(7)-Ba(3)-O(3)$ $47.74(10)$ $F(2)#9-Ba(3)-O(5)$ $78.87(14)$ $O(9)#5-Ba(3)-O(3)$ $104.80(10)$ $F(2)-Ba(3)-O(7)$ $104.01(12)$ $O(1)-Ba(3)-O(3)$ $45.84(10)$ $F(2)#9-Ba(3)-O(7)$ $95.56(12)$ $O(5)#9-Ba(3)-O(3)$ $68.63(11)$ $O(5)-Ba(3)-O(7)$ $141.57(10)$ $O(10)#5-Ba(3)-O(3)$ $128.00(10)$ $F(2)-Ba(3)-O(9)#5$ $107.44(13)$ $O(6)#10-Ba(3)-O(3)$ $118.79(9)$ $F(2)#9-Ba(3)-O(9)#5$ $73.31(13)$ $F(2)-Ba(3)-O(4)#10$ $72.85(12)$	)#6-Ba(2)-O(3)#5 4	47.89(11)	F(2)-Ba(3)-O(3)	69.11(14)
F(2)-Ba(3)-F(2)#9154.68(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)#5107.44(13) $O(6)$ #10-Ba(3)-O(3)118.79(9) $F(2)$ #9-Ba(3)-O(9)#573.31(13) $F(2)$ -Ba(3)-O(4)#1072.85(12) $O(5)$ P $O(2)$ $O(2)$ #5 $O(2)$ #0 $P(2)$ #0 $O(2)$ $O(4)$ #10 $O(2)$	#7-Ba(2)-O(3)#5	120.53(10)	F(2)#9-Ba(3)-O(3)	135.94(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)#5107.44(13) $O(6)$ #10-Ba(3)-O(3)118.79(9) $F(2)$ #9-Ba(3)-O(9)#573.31(13) $F(2)$ -Ba(3)-O(4)#1072.85(12) $O(5)$ P. (2) $O(2)$ #501.24(11) $E(2)$ #0 P. (2) $O(4)$ #10105.48(12)	Ba(3)-F(2)#9	154.68(12)	O(5)-Ba(3)-O(3)	144.35(14)
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)#5107.44(13) $O(6)$ #10-Ba(3)-O(3)118.79(9) $F(2)$ #9-Ba(3)-O(9)#573.31(13) $F(2)$ -Ba(3)-O(4)#1072.85(12) $O(5)$ P $O(2)$ $O(2)$ #5 $O(2)$ #5 $O(2)$ #5	Ba(3)-O(5) 7	75.81(13)	O(7)-Ba(3)-O(3)	47.74(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)#5107.44(13)O(6)#10-Ba(3)-O(3)118.79(9) $F(2)$ #9-Ba(3)-O(9)#573.31(13) $F(2)$ -Ba(3)-O(4)#1072.85(12)O(5) P. (2) O(2)#501.24(11) $F(2)$ -Ba(3)-O(4)#1072.85(12)	9-Ba(3)-O(5)	78.87(14)	O(9)#5-Ba(3)-O(3)	104.80(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)#5107.44(13) $O(6)$ #10-Ba(3)-O(3)118.79(9) $F(2)$ #9-Ba(3)-O(9)#573.31(13) $F(2)$ -Ba(3)-O(4)#1072.85(12) $O(5)$ P. (2) $O(9)$ #501.24(11) $F(2)$ -Ba(3)-O(4)#10105.48(12)	Ba(3)-O(7)	104.01(12)	O(1)-Ba(3)-O(3)	45.84(10)
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)#5107.44(13) $O(6)$ #10-Ba(3)-O(3)118.79(9) $F(2)$ #9-Ba(3)-O(9)#573.31(13) $F(2)$ -Ba(3)-O(4)#1072.85(12) $O(5)$ P. (2) $O(9)$ #501.24(11) $F(2)$ -Ba(3)-O(4)#10105.48(12)	9-Ba(3)-O(7)	95.56(12)	O(5)#9-Ba(3)-O(3)	68.63(11)
F(2)-Ba(3)-O(9)#5107.44(13)O(6)#10-Ba(3)-O(3)118.79(9) $F(2)$ #9-Ba(3)-O(9)#573.31(13) $F(2)$ -Ba(3)-O(4)#1072.85(12) $O(5)$ P. (2) $O(9)$ #501.24(11) $F(2)$ -Ba(3)-O(4)#10105.48(12)	-Ba(3)-O(7) 1	141.57(10)	O(10)#5-Ba(3)-O(3)	128.00(10)
F(2)#9-Ba(3)-O(9)#5 73.31(13) $F(2)-Ba(3)-O(4)#10$ 72.85(12)	Ba(3)-O(9)#5	107.44(13)	O(6)#10-Ba(3)-O(3)	118.79(9)
O(5) D(2) O(0)    5 = 0.1.24(11) D(2) O(4)    10 = 105.49(12)	<sup>49</sup> -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)	·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)	-Ba(3)-O(9)#5 1	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)	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	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)	-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  $Ba_3B_6O_{11}F_2$ .