Supplementary materials for:

Synthesis, structural characterization and scalable preparation of new amino-zinc borates.

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1. Crystallographic supplementary information.

Table S1. Crystal data, data collection, structure determination and refinement for ZB1.

Chemical formula	$B_4H_{15}N_3O_{10}Zn$	
Formula weight	325.76 g/mol	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal size	0.166 x 0.176 x 0.216 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 12.215(4) Å	α = 90°
	b = 7.845(3) Å	β = 107.323(15)°
	c = 12.172(4) Å	γ = 90°
Volume	1113.5(6) $Å^3$	
Z	4	
Density (calculated)	1.943 g/cm^3	
Absorption coefficient	2.256 mm^{-1}	
F(000)	664	
Theta range for data collection	3.13 to 33.20°	
Index ranges	-18<=h<=18, -10<=k<=11, -18<=l<=18	
Reflections collected	5167	
Independent reflections	3344 [R(int) = 0.0184]	
Coverage of independent reflections	92.5%	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3344 / 5 / 181	
Goodness-of-fit on F2	1.064	
Δ/σmax	0.0	
Final R indices	3033 data; I>2σ(I)	R1 = 0.0308, wR2 = 0.0698
	all data	R1 = 0.0379, wR2 = 0.0729
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0393P)^2+0.3251P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.281(14)	
Largest diff. peak and hole	0.339 and -0.421 $eÅ^{-3}$	
R.M.S. deviation from mean	0.078 $eÅ^{-3}$	

Table S2. Crystal data, data collection, structure determination and refinement for ZB3.

Chemical formula	$ZnB_4O_{13}N_4H_{24}$
Formula weight	396.84 g/mol

Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal size	0.195 x 0.231 x 0.232 mm	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 15.0796(9) Å	α = 90°
	b = 11.8853(5) Å	β = 90°
	c = 16.7606(8) Å	γ = 90°
Volume	3003.9(3) $Å^3$	
Z	8	
Density (calculated)	1.755 g/cm^3	
Absorption coefficient	1.705 mm^{-1}	
F(000)	1648	
Theta range for data collection	3.20 to 30.62°	
Index ranges	-21<=h<=21, -16<=k<=17, -23<=l<=23	
Reflections collected	100416	
Independent reflections	4605 [R(int) = 0.0475]	
Coverage of independent reflections	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7320 and 0.6930	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4605 / 35 / 233	
Goodness-of-fit on F2	1.059	
Δ/σmax	0.001	
Final R indices	3806 data; I>2σ(I)	R1 = 0.0298, wR2 = 0.0658
	all data	R1 = 0.0421, wR2 = 0.0725
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0298P)^2+2.0035P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.260 and -0.569 $eÅ^{-3}$	
R.M.S. deviation from mean	0.067 $eÅ^{-3}$	

Table S3. Crystallographic information for ZB1.

Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for ZB1.				
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.				
	x/a	y/b	z/c	U(eq)
Zn01	0.48531(3)	0.69468(4)	0.55678(3)	0.01877(9)
N1	0.3228(3)	0.6740(4)	0.4550(3)	0.0246(6)
N2	0.4998(5)	0.8243(5)	0.7052(4)	0.0417(10)
N3	0.5876(3)	0.8307(4)	0.4835(3)	0.0238(6)
O1	0.52666(19)	0.4552(3)	0.5928(2)	0.0142(4)
B1	0.5696(3)	0.3385(5)	0.5177(3)	0.0133(6)
B2	0.4749(3)	0.3544(4)	0.6692(3)	0.0134(6)
O2	0.60068(19)	0.4297(3)	0.4293(2)	0.0211(5)
B3	0.3878(3)	0.1861(4)	0.4972(3)	0.0149(6)
O3	0.4796(2)	0.2161(3)	0.4594(2)	0.0190(5)
O4	0.43232(19)	0.4585(3)	0.7433(2)	0.0194(5)
B4	0.6553(3)	0.1872(4)	0.6972(3)	0.0161(6)
O5	0.6684(2)	0.2442(3)	0.5954(2)	0.0192(5)
O8	0.7323(2)	0.0772(4)	0.7658(2)	0.0294(6)
O7	0.3747(2)	0.2576(4)	0.5943(2)	0.0184(5)
O6	0.3041(2)	0.0742(4)	0.4393(2)	0.0266(6)
O9	0.5631(2)	0.2317(3)	0.7332(2)	0.0178(5)
O1W	0.2723(3)	0.9201(5)	0.2323(3)	0.0516(10)
		Bond lengths (Å) for ZB1.		

Zn01-O1	1.961(2)	Zn01-N1	2.009(3)
Zn01-N2	2.034(4)	Zn01-N3	2.039(3)
N1-H1A	0.89	N1-H1B	0.89
N1-H1C	0.89	N2-H2A	0.89
N2-H2B	0.89	N2-H2C	0.89
N3-H3A	0.89	N3-H3B	0.89
N3-H3C	0.89	O1-B1	1.496(4)
O1-B2	1.497(4)	B1-O2	1.434(4)
B1-O3	1.473(4)	B1-O5	1.489(4)
B2-O4	1.425(4)	B2-O9	1.481(4)
B2-O7	1.497(4)	O2-H2	0.82
B3-O3	1.353(4)	B3-O7	1.361(4)
B3-O6	1.373(4)	O4-H4	0.82
B4-O8	1.363(4)	B4-O9	1.369(4)
B4-O5	1.371(4)	O8-H8	0.82
O6-H6	0.82	O1W-H1WA	0.8456
O1W-H1WB	0.8782		
		Bonds angles for ZB1.	
O1-Zn01-N1	101.65(11)	O1-Zn01-N2	109.36(14)
N1-Zn01-N2	113.37(18)	O1-Zn01-N3	116.65(11)
N1-Zn01-N3	113.21(14)	N2-Zn01-N3	102.96(15)
Zn01-N1-H1A	109.5	Zn01-N1-H1B	109.5
H1A-N1-H1B	109.5	Zn01-N1-H1C	109.5
H1A-N1-H1C	109.5	H1B-N1-H1C	109.5
Zn01-N2-H2A	109.5	Zn01-N2-H2B	109.5
H2A-N2-H2B	109.5	Zn01-N2-H2C	109.5
H2A-N2-H2C	109.5	H2B-N2-H2C	109.5
Zn01-N3-H3A	109.5	Zn01-N3-H3B	109.5
H3A-N3-H3B	109.5	Zn01-N3-H3C	109.5
H3A-N3-H3C	109.5	H3B-N3-H3C	109.5
B1-O1-B2	110.3(2)	B1-O1-Zn01	124.30(19)
B2-O1-Zn01	121.14(17)	O2-B1-O3	106.9(3)
O2-B1-O5	112.3(3)	O3-B1-O5	109.2(3)
O2-B1-O1	111.9(3)	O3-B1-O1	110.2(2)
O5-B1-O1	106.3(3)	O4-B2-O9	112.7(3)
O4-B2-O1	113.1(3)	O9-B2-O1	107.1(2)
O4-B2-O7	106.8(2)	O9-B2-O7	109.0(3)
O1-B2-O7	108.1(3)	B1-O2-H2	109.5
O3-B3-O7	123.2(3)	O3-B3-O6	120.2(3)
O7-B3-O6	116.5(3)	B3-O3-B1	121.7(3)
B2-O4-H4	109.5	O8-B4-O9	116.7(3)
O8-B4-O5	121.0(3)	O9-B4-O5	122.3(3)
B4-O5-B1	116.5(2)	B4-O8-H8	109.5
B3-O7-B2	116.8(2)	B3-O6-H6	109.5
B4-O9-B2	122.5(2)	H1WA-O1W-H1WB	108.6

Table S4. Crystallographic information for ZB3.

Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for ZB3.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Zn01	0.64100(2)	0.81241(2)	0.61493(2)	0.02704(6)
N1	0.75516(10)	0.88183(12)	0.57680(8)	0.0310(3)
N2	0.53783(10)	0.89410(13)	0.56541(9)	0.0365(3)
N3	0.63415(9)	0.64769(12)	0.59063(8)	0.0276(3)
N4	0.62220(9)	0.83981(14)	0.73239(8)	0.0331(3)
O1	0.43022(6)	0.73177(8)	0.67617(6)	0.01678(18)
O2	0.41881(7)	0.85883(9)	0.79030(6)	0.0232(2)
O3	0.31594(7)	0.71137(8)	0.77535(6)	0.01855(19)

O4	0.43175(7)	0.60471(9)	0.56323(6)	0.0255(2)
B1	0.37278(9)	0.79241(12)	0.73115(8)	0.0152(3)
B2	0.37859(10)	0.67322(12)	0.61597(9)	0.0164(3)
B3	0.28770(10)	0.61942(12)	0.73447(9)	0.0169(3)
O5	0.31279(7)	0.86890(8)	0.68358(6)	0.01938(19)
O6	0.23341(8)	0.54600(9)	0.77387(6)	0.0268(2)
O9	0.32908(7)	0.75723(9)	0.56589(6)	0.0208(2)
O7	0.31055(7)	0.59981(8)	0.65626(6)	0.0208(2)
B4	0.29605(10)	0.84939(13)	0.60460(9)	0.0171(3)
O8	0.24367(8)	0.92187(9)	0.56194(6)	0.0270(2)
O1W	0.52439(8)	0.86655(11)	0.92272(7)	0.0313(3)
O2W	0.49068(10)	0.06004(11)	0.73426(9)	0.0416(3)
O3W	0.38695(14)	0.62417(15)	0.92194(8)	0.0585(5)
O4W	0.38569(12)	0.16406(16)	0.60684(11)	0.0542(4)

Bond lengths (Å) for ZB3.

Zn01-N3	2.0023(14)	Zn01-N2	2.0131(15)
Zn01-N1	2.0132(14)	Zn01-N4	2.0154(14)
N1-H1A	0.89	N1-H1B	0.89
N1-H1C	0.89	N2-H2A	0.89
N2-H2B	0.89	N2-H2C	0.89
N3-H3A	0.89	N3-H3B	0.89
N3-H3C	0.89	N4-H4A	0.89
N4-H4B	0.89	N4-H4C	0.89
O1-B2	1.4520(17)	O1-B1	1.4556(17)
O2-B1	1.4451(17)	O2-H2	0.782(15)
O3-B3	1.3584(17)	O3-B1	1.4870(17)
O4-B2	1.4447(17)	O4-H4	0.82
B1-O5	1.5101(17)	B2-O9	1.5030(18)
B2-O7	1.5067(17)	B3-O6	1.3667(17)
B3-O7	1.3752(17)	O5-B4	1.3675(17)
O6-H6	0.804(15)	O9-B4	1.3671(18)
B4-O8	1.3702(18)	O8-H8	0.811(15)
O1W-H1WA	0.779(14)	O1W-H1WB	0.772(14)
O2W-H2WA	0.796(15)	O2W-H2WB	0.791(15)
O3W-H3WA	0.776(16)	O3W-H3WB	0.773(16)
O4W-H4WA	0.779(16)	O4W-H4WB	0.778(16)

Bonds angles for ZB3.

N3-Zn01-N2	110.35(6)	N3-Zn01-N1	112.35(6)
N2-Zn01-N1	109.41(6)	N3-Zn01-N4	110.45(6)
N2-Zn01-N4	102.48(6)	N1-Zn01-N4	111.35(6)
Zn01-N1-H1A	109.5	Zn01-N1-H1B	109.5
H1A-N1-H1B	109.5	Zn01-N1-H1C	109.5
H1A-N1-H1C	109.5	H1B-N1-H1C	109.5
Zn01-N2-H2A	109.5	Zn01-N2-H2B	109.5
H2A-N2-H2B	109.5	Zn01-N2-H2C	109.5
H2A-N2-H2C	109.5	H2B-N2-H2C	109.5
Zn01-N3-H3A	109.5	Zn01-N3-H3B	109.5
H3A-N3-H3B	109.5	Zn01-N3-H3C	109.5
H3A-N3-H3C	109.5	H3B-N3-H3C	109.5
Zn01-N4-H4A	109.5	Zn01-N4-H4B	109.5
H4A-N4-H4B	109.5	Zn01-N4-H4C	109.5
H4A-N4-H4C	109.5	H4B-N4-H4C	109.5
B2-O1-B1	110.98(10)	B1-O2-H2	109.5
B3-O3-B1	116.78(10)	B2-O4-H4	109.5
O2-B1-O1	114.77(11)	O2-B1-O3	106.79(11)
O1-B1-O3	109.74(10)	O2-B1-O5	108.73(11)
O1-B1-O5	108.69(10)	O3-B1-O5	107.92(10)
O4-B2-O1	113.44(12)	O4-B2-O9	107.96(11)
O1-B2-O9	109.64(11)	O4-B2-O7	109.01(11)

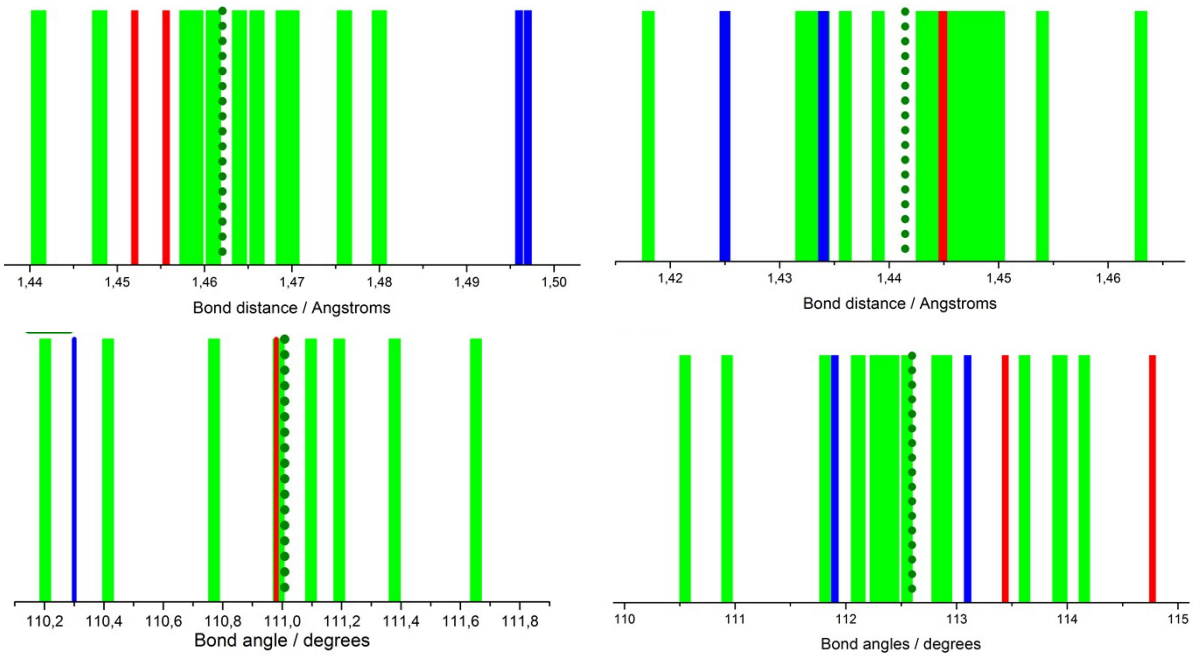
O1-B2-O7	109.34(10)	O9-B2-O7	107.26(11)
O3-B3-O6	117.24(12)	O3-B3-O7	122.58(12)
O6-B3-O7	120.16(12)	B4-O5-B1	121.30(11)
B3-O6-H6	109.5	B4-O9-B2	116.63(10)
B3-O7-B2	119.98(11)	O9-B4-O5	121.88(12)
O9-B4-O8	117.78(12)	O5-B4-O8	120.33(12)
B4-O8-H8	109.5	H1WA-O1W-H1WB	107.(2)
H2WA-O2W-H2WB	102.(2)	H3WA-O3W-H3WB	107.(3)
H4WA-O4W-H4WB	108.(2)		
N3-Zn01-N2	110.35(6)	N3-Zn01-N1	112.35(6)
N2-Zn01-N1	109.41(6)	N3-Zn01-N4	110.45(6)

2. Statistical study for ZB1 and ZB3 parameters.

Table S5. Result from database search for compounds containing tetraborate ion.

Entries	Database Code CSD	Study Temp.	R-factor
1	AYOLIJ	296	2.28
2	BOJWIG01	295	3.4
3	BOJWIG10	295	3.3
4	BOJWIG11	295	3.4
5	CUGNAT	295	5.2
6	DALQEN	293	3.99
7	HAGSEN	295	4.6
8	SIBDIR	294	4.93
9	WEZSEZ01	293	4.23
10	YURJOL	294	5.56
11	BOJWIG	295	3.3
12	HAGSEN01	295	5.7
13	WEZSEZ*	295	7.3
14	OSURUR*	145	2.46
15	BAZQEA*	120	8.96
16	RINZEU*	260	6.37

* Entries 13, 14, 15 and 16 were not used for statistical study.



FigureS1. Comparison of ZB1 and ZB3 parameters with literature values. (top left) B1-O1 and B2-O1 bond distances- (bottom-left) B1-O1-B2 bond angle. (top-right), B1-O2 and B2-O4 bond distances. (bottom-right) O2-B1-O1 and O1-B2-O4 bond angles. Colors code for parameters is: blue for ZB1, red for ZB3, green for reported compounds in CSD and dot-olive for average data of reported compounds in CSD.

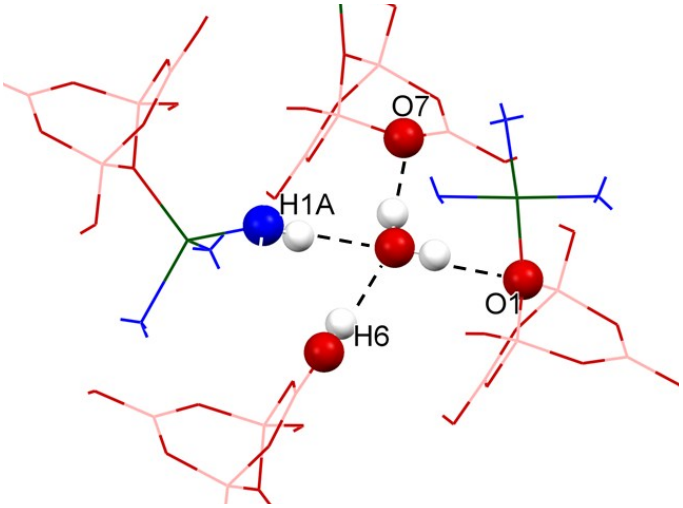


Figure S2. H-bonds formed by the water molecule in the crystal network of ZB1.

Table S6. H-bonds (Å, °) in ZB1.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N1-H1A···O6	0.89	2.59	3.149(4)	122.0
N1-H1A···O1W	0.89	2.35	3.235(5)	171.4
N1-H1B···O5	0.89	2.06	2.949(4)	177.0
N1-H1C···O8	0.89	2.21	2.983(4)	144.8
N2-H2B···O9	0.89	2.42	3.282(4)	162.4
N2-H2C···O2	0.89	2.52	3.305(5)	148.0
N3-H3A···O7	0.89	2.54	3.410(4)	167.1
N3-H3B···O3	0.89	2.40	3.277(4)	166.8
N3-H3C···O9	0.89	2.14	3.012(4)	166.7
O2-H2···O6	0.82	1.95	2.700(3)	152.5
O4-H4···O2	0.82	1.89	2.711(4)	175.1
O8-H8···O4	0.82	2.15	2.703(3)	125.3
O6-H6···O1W	0.82	1.97	2.717(4)	151.2
O1W-H1WA···O7	0.85	1.92	2.753(4)	169.8
O1W-H1WB···O1	0.88	2.29	3.131(4)	159.5
O1W-H1WB···O5	0.88	2.50	3.172(5)	134.1

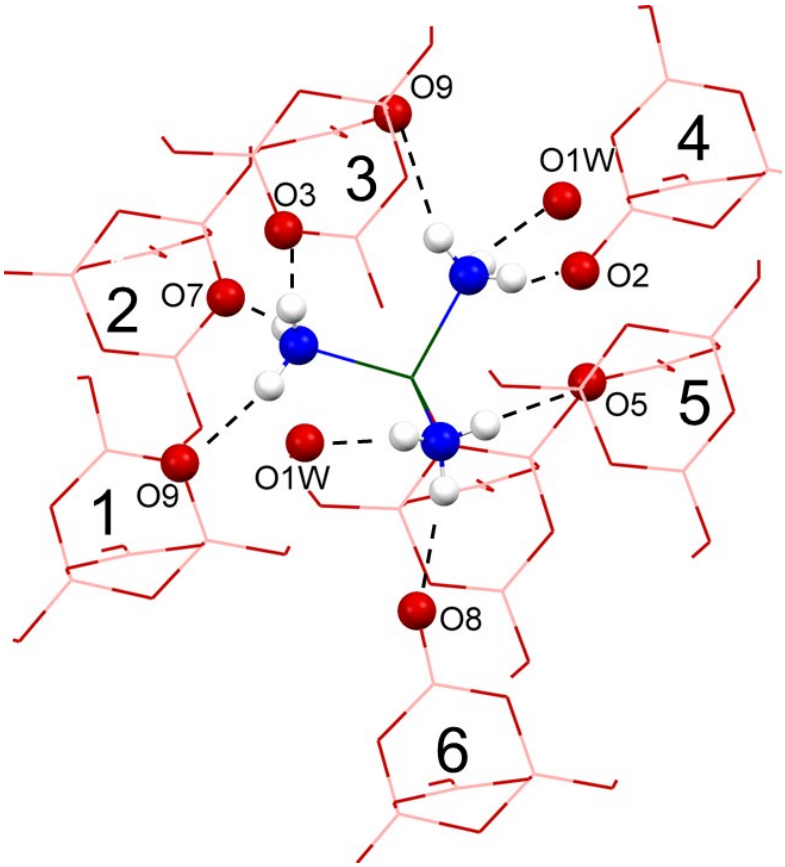


Figure S3. Connections for ammonia molecules in the crystal network of ZB1. Different units of tetraborates are indicated with numbers.

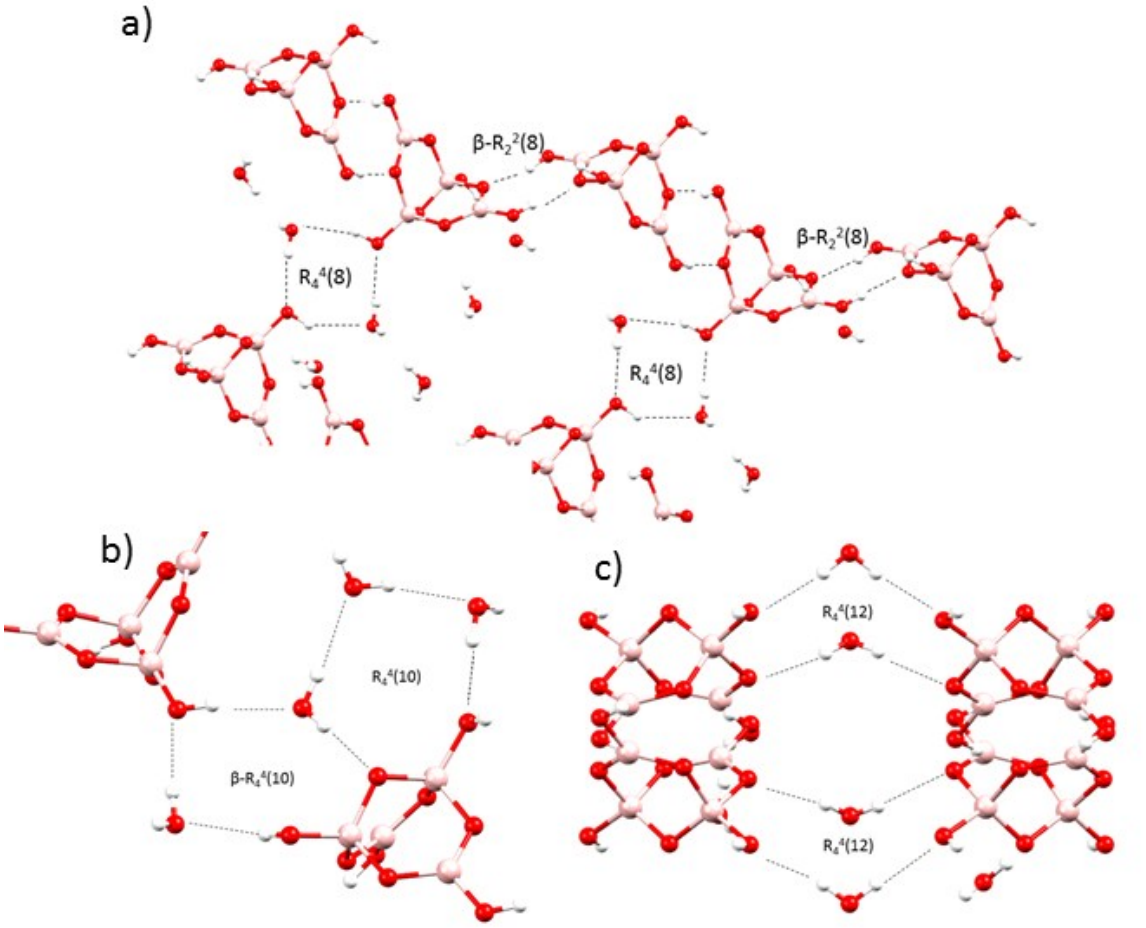


Figure S4. H-bond motifs found in ZB3 structure. The H-bond pattern are named using the nomenclature developed by Etter. The interactions between the tetraborates anions are described using the α, β, γ nomenclature system of Schubert (Visi et al, 2006). A redefinition of the three types of oxygens was needed in order to adapt the nomenclature for the tetraborates α (O3, O5, O7 and O9), β (O2, O4, O6 and O8) and γ (O1).

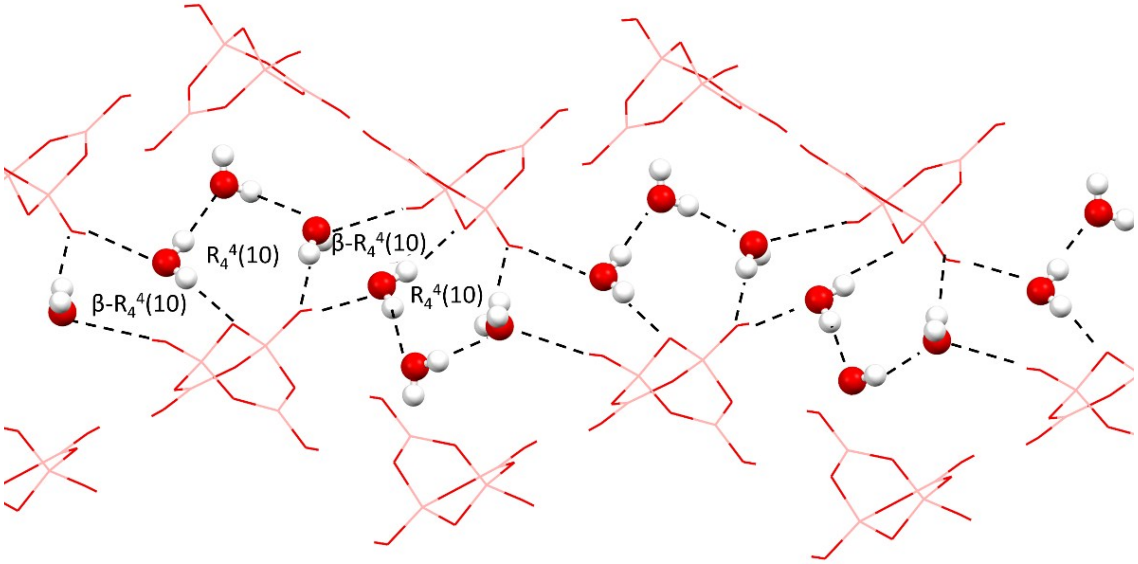


Figure S5. β-R_4^4(10) and R_4^4(10) motifs connecting two chains of β-R_2^2(8) belonging to one brickwall.

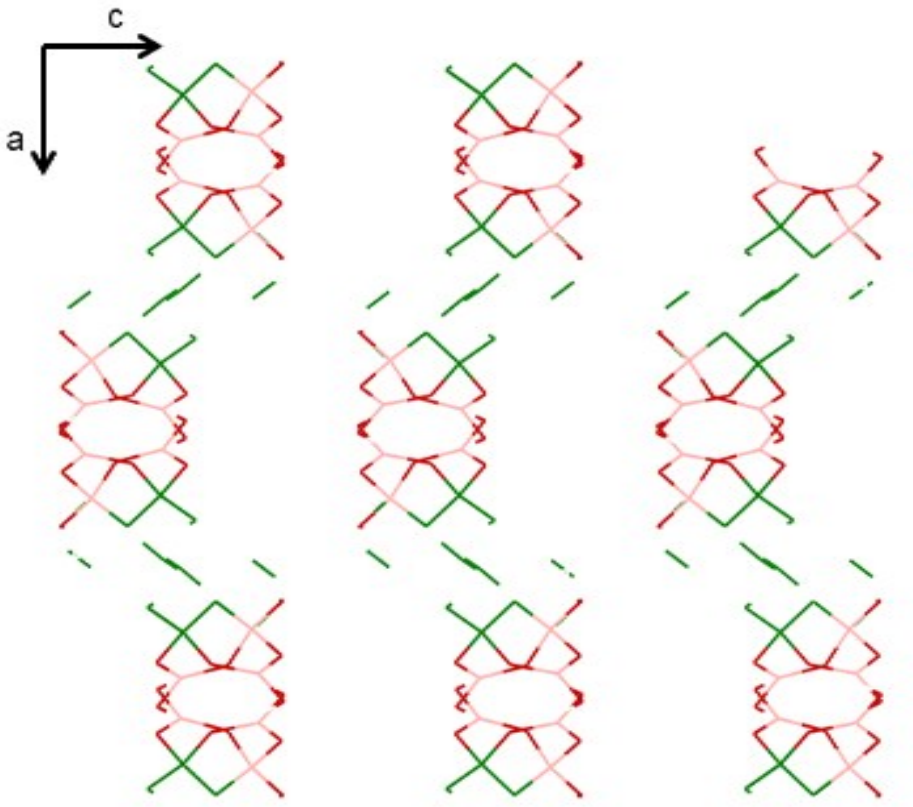


Figure S6. Motifs $R_4^4(10)$ connecting chains between brickwalls in the structure of ZB3. The atoms involved are depicted in green.

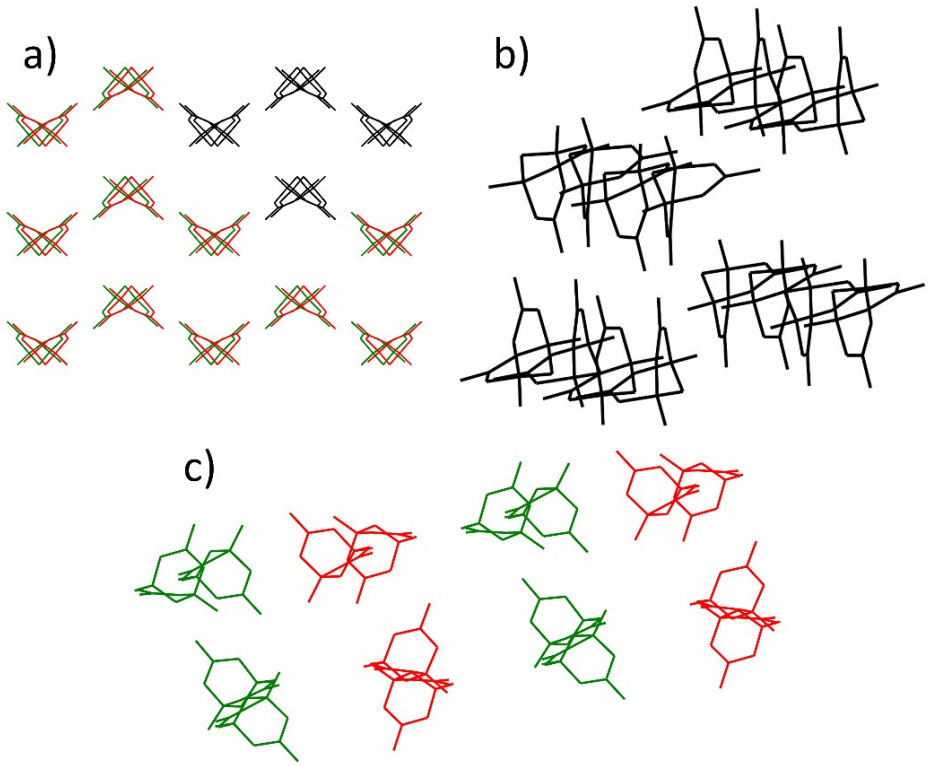


Figure S7. a) Single brickwall in plane *ab* . b) Tetraborate anions of one of the channels along *c*-axis shown in black. C) Another view of the channel showing tetraborates belonging to different brickwalls (green and red).

Table S7. DFT calculated energies for H-bond motifs found in ZB3 (B3LYP-6-311++G(d,p) optimized geometries). Relative energy is estimated as the difference between the energy of the motif and the energy of the H_2O and $B_4O_9H_4^{2-}$ species involved. ER = Electrostatic repusion between anions.

Entries	Specie / Motif	Absolute Energy (kJ/mol)	Relative Energy (kJ/mol)	H-Bond energy + ER (kJ/mol)
1	$B_4O_9H_4^{2-}$	-2047800	0	-
2	H_2O	-200720.0178	0	-
3	β-$R_2^2(8)$	-4095614.682	-14.68164251	-7.340821255
4	$R_4^4(8)$	-4497056.311	-16.27530435	-4.068826087
5	β-$R_4^4(10)$	-4497057.747	-17.71143784	-4.427859459
6	$R_4^4(10)$	-2649991.391	-31.33764038	-7.834410095
7	$R_4^4(12)$	-4497059.155	-19.11869112	-4.779672781

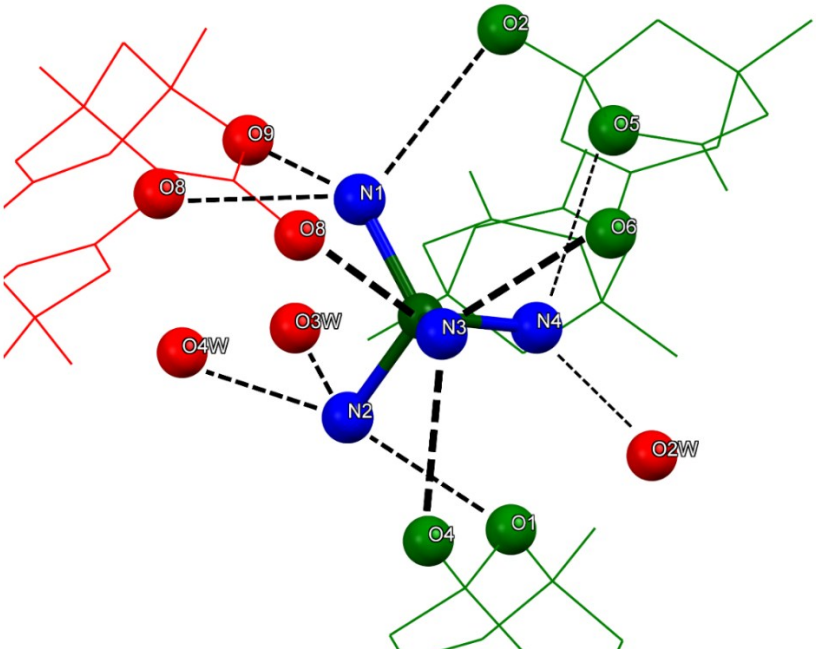


Figure S8. Connections for ammonia molecules in the crystal network of ZB3. Two different "brickwalls" are shown in green and red.

Table S8. H-bond geometry (Å, °) for ZB3.

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
N1-H1A···O9	0.89	2.22	3.1134(17)	179.3
N1-H1B···O2	0.89	2.46	3.3355(19)	168.9
N1-H1C···O8	0.89	2.55	3.2940(18)	141.6
N2-H2A···O3W	0.89	2.13	2.968(2)	155.7
N2-H2B···O1	0.89	2.38	3.1308(19)	142.1
N2-H2C···O4W	0.89	2.39	3.185(3)	149.1
N3-H3A···O8	0.89	2.27	3.1543(18)	171.3
N3-H3B···O4	0.89	2.25	3.1284(18)	169.2
N3-H3C···O6	0.89	2.1	2.9764(17)	169.3
N4-H4A···O3	0.89	2.64	3.2988(18)	131.9
N4-H4A···O5	0.89	2.36	3.2191(18)	161.5
N4-H4C···O2W	0.89	2.46	3.284(2)	154.3
O2-H2···O2W	0.78	2.02	2.7886(17)	169.2
O4-H4···O1W	0.82	2.16	2.9163(17)	153.3
O6-H6···O5	0.8	1.89	2.6843(14)	171.3
O8-H8···O7	0.81	1.95	2.7642(14)	177.0
O1W-H1WA···O2	0.779(14)	1.960(15)	2.7329(15)	172.(3)
O1W-H1WB···O4	0.772(14)	1.994(15)	2.7594(15)	171.(2)
O2W-H2WA···O4W	0.796(15)	2.138(15)	2.932(2)	174.(3)
O2W-H2WB···O1	0.791(15)	2.013(15)	2.8005(16)	174.(3)
O3W-H3WA···O3	0.776(16)	2.102(17)	2.8736(18)	173.(4)
O3W-H3WB···O9	0.773(16)	2.163(18)	2.9273(18)	170.(4)
O4W-H4WA···O7	0.779(16)	2.50(2)	3.166(2)	145.(3)
O4W-H4WB···O1W	0.778(16)	2.060(18)	2.806(2)	161.(3)

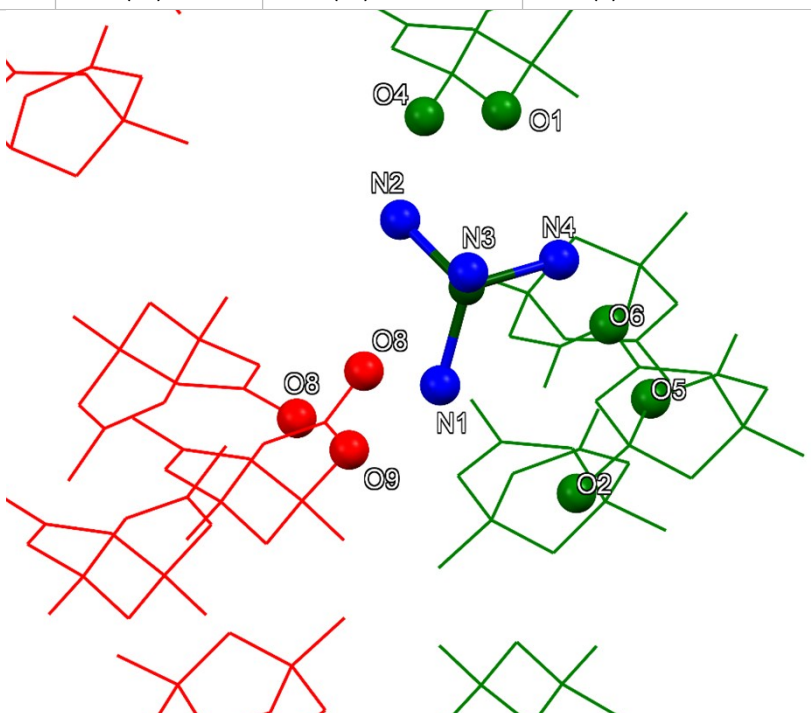


Figure S9. Tetra amino-Zn cation connecting two brickwalls.

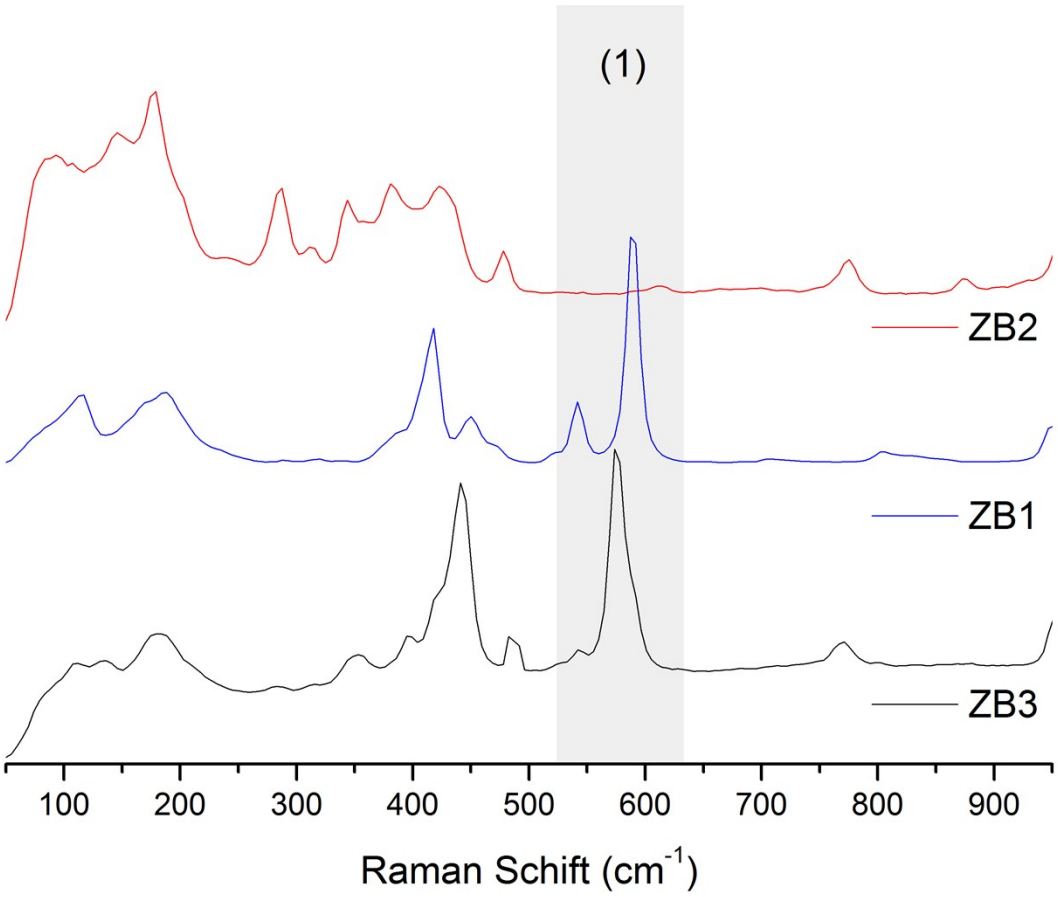


Figure S10. Experimental Raman spectra of ZB1, ZB2 and ZB3. Zone (1) shows the absence of ν(Zn01-O1), ν_S(B1-O1) and ν_S(B2-O1) vibrational modes in the Raman spectrum of ZB2 (see Figure S14, S17 and Table S12, S14).

3. Indexing information for ZB2.

Table S9. Structural parameters.

a	b	c	α	β	γ	Vol (Å)	Rp	Rwp	χ^2
36.78076 (6)	36.780762 (6)	12.20052 (3)	90	90	120	14306.0	0.0637	0.0782	3.143

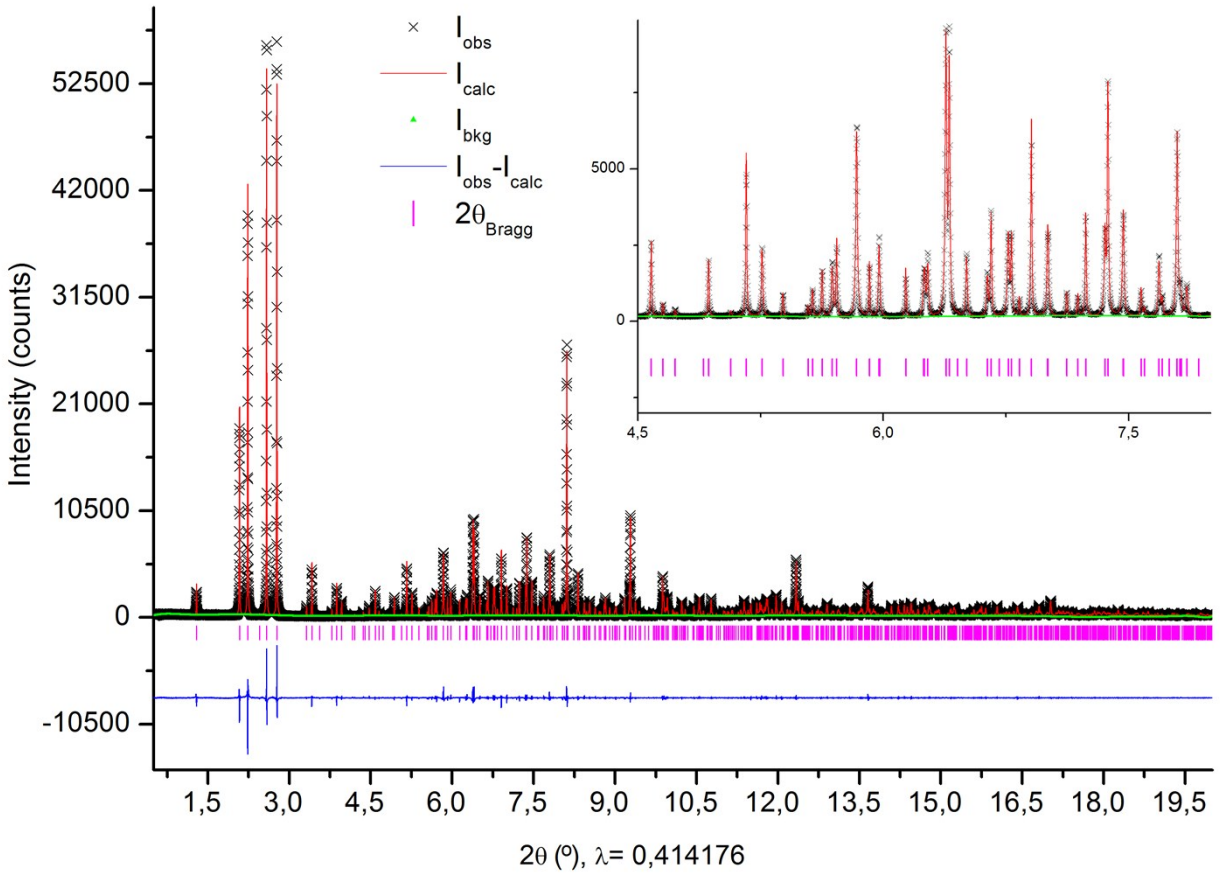


Figure S11. Le Bail fit.

4. Infrared and Raman support information

Table S10. Performance of the applied computational methods.

ZB1		RMSD
Experimental		0
Method	Basis set	
DFT (B3LYP)	6-311++Gdp	1,2591
	6-31Gdp	1,6160
DFT (M062X)	6-311++Gdp	1,7518
	6-31Gdp	1,9477
MP2	6-311++Gdp	1,5014
	6-31Gdp	1,9442
HF	6-311++Gdp	1,3464
	6-31Gdp	1,6857

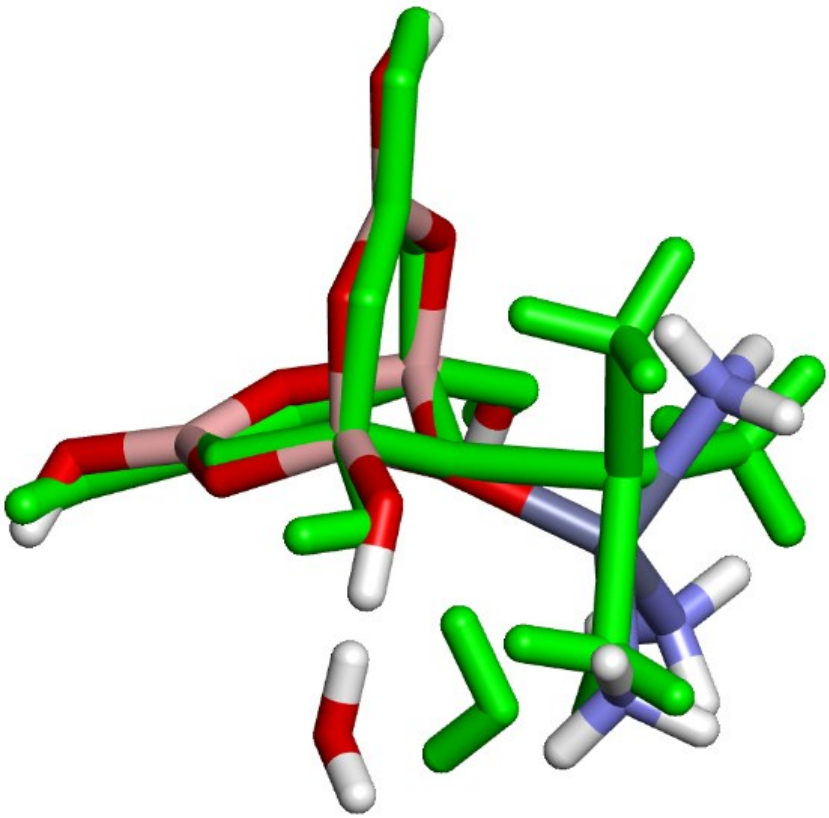


Figure S12. RB3LYP/6-311++G(d,p) optimized structure for ZB1. The crystal structure is shown superimposed in green.

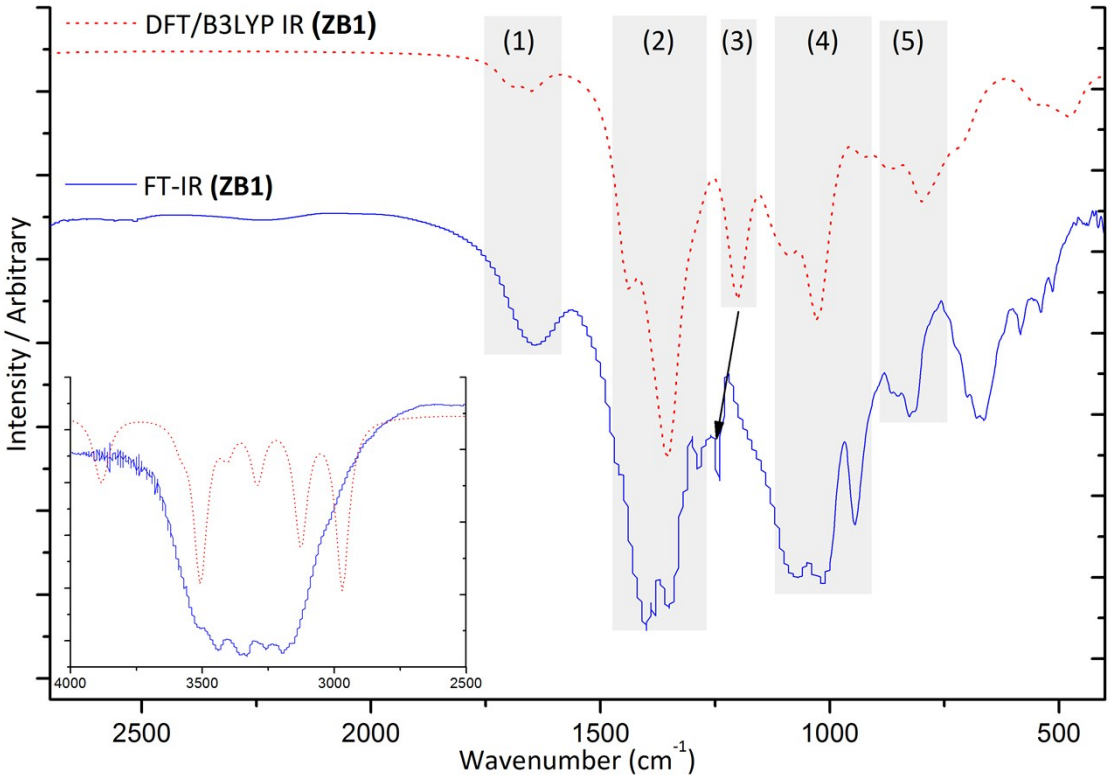


Figure S13. Experimental and DFT calculated infrared spectra for ZB1.

Table S11. Infrared normal modes assignment for ZB1.

Zone (See Fig. S13)	DFT/B3LYP (cm^{-1})	FT-IR (cm^{-1})	Assignment
1	1648	1639	σ H1WA-O1W-H1WB + σ H1A-N1-H1B + σ H2A-N2-H2B + σ H3A-N3-H3C
2	1441	1459	ν_{as} O9-B4-O5+ ν_{as} O3-B3-O7+ σ B3-O6-H6 + σ B4-O8-H8
	1348	1349	ν_{as} O8-B4-O9+ ν_{as} O6-B3-O7 + ω $(N1)H_3$+ ω $(N2)H_3$
	1389	1391	ν_{as}O8-B4-O5+ ω$(N2)H_3$ + ν_{as} O6-B3-O7 +σ B3-O6-H6
3	1201	1239	σ B1-O2-H2+ σ B2-O4-H4
4	1088	1084	ν_{as} O2-B1-O3+ ν_{as} O7-B2-O4 + ρH8 + ρH2 + ρH6
	1029	1022	ν_{as} O9-B2-O4 + ρH8
	928	942	ν_{as} O9-B2-O7 + ν_{as} O5-B1-O3 + ρHX (X=2,4,6,8)
5	855	859	ν_{s} B4-O + ν_{s} B3-O
	801	818	ρ N1-$(H)_3$

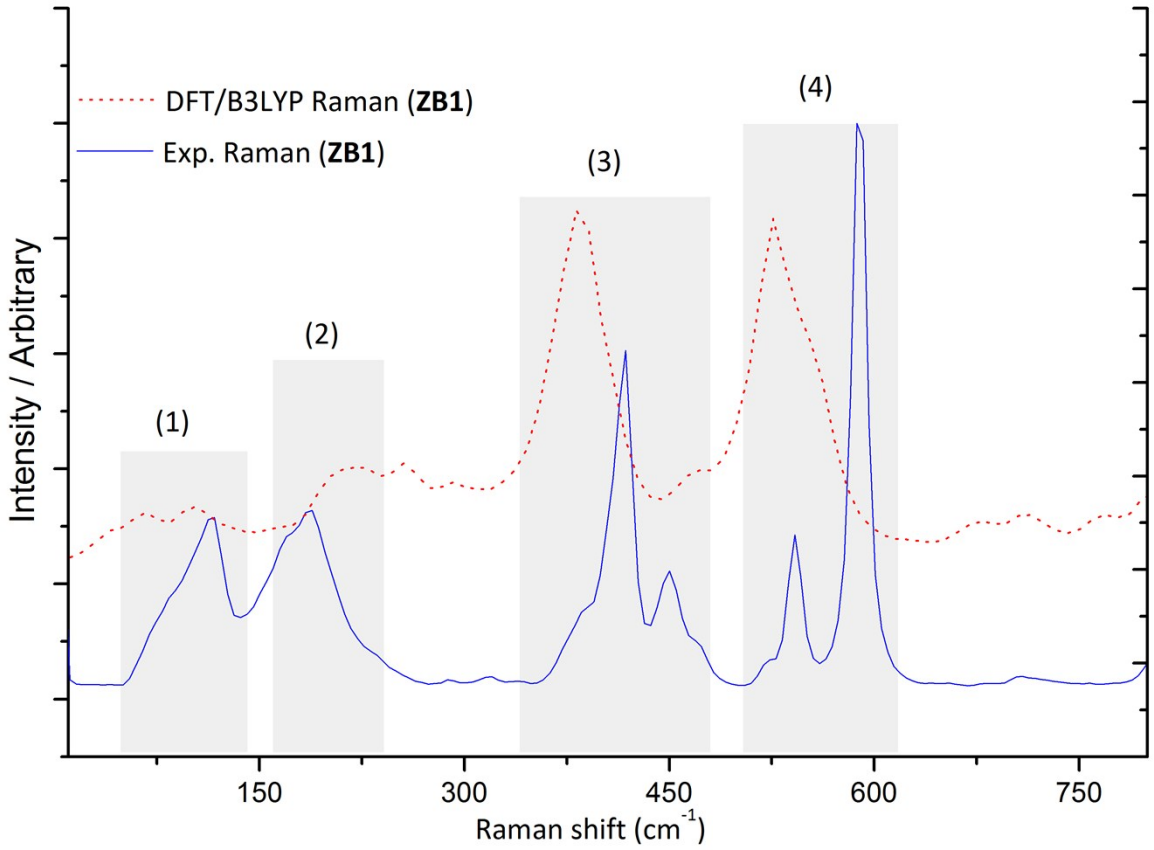


Figure S14. Experimental and DFT calculated Raman spectra for ZB1.

Table S12. Active Raman modes assignment for ZB1.

Zone (Fig. S14)	DFT/B3LYP (cm^{-1})	Raman shift (cm^{-1})	Assignment
1	66	76	ω H6-(O8-B4) + ω H6-(O6-B3)
	113	115	δ Zn-$(N)_3$
2	200	185	ρ of the H bonding to O1W + τ NH_3
3	388	386	Asymmetric ring breathing
	373	383-415	ν Zn01-N2
	384		ν Zn01-N3
	407		ν Zn01-N1
	461	451	σ O3-B3-O7
4	525	523	ν Zn01-O1 + $ν_s$ B1-O + $ν_s$ B2-O
	548	541	σ (H6O6)-B3-O3 + σ (H8O8)-B4-O9
	560	589	σ O5-B4-O9

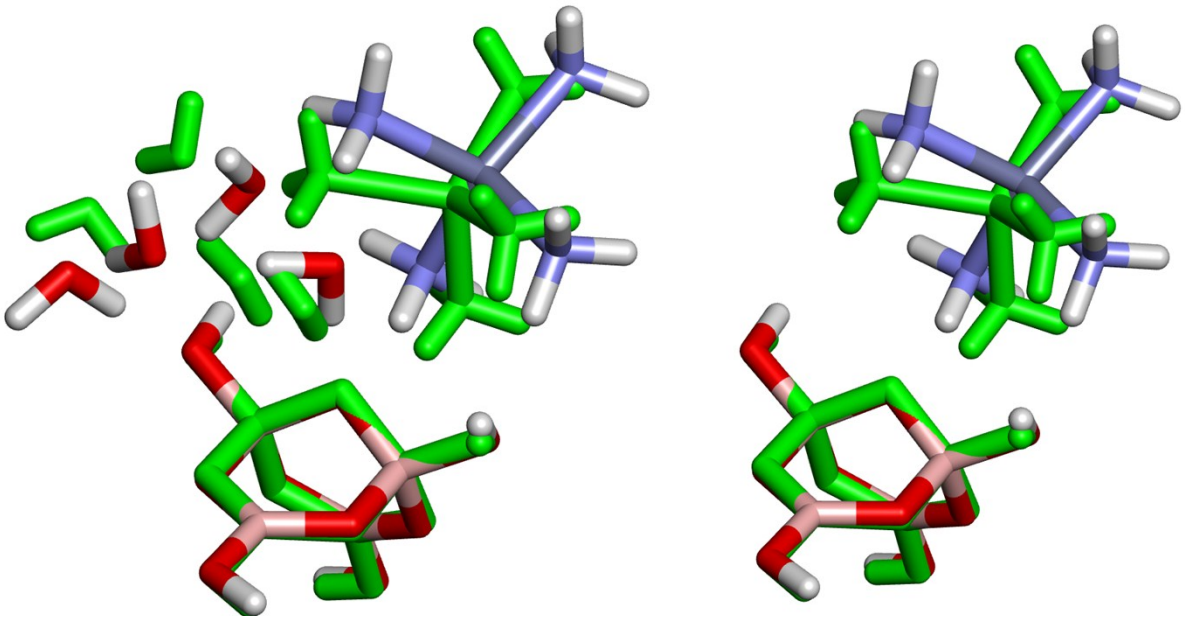


Figure S15. RB3LYP/6-311++G(d,p) optimized structure for ZB3. The crystal structure is shown superimposed in green. (Right) Water molecules were excluded for clarity.

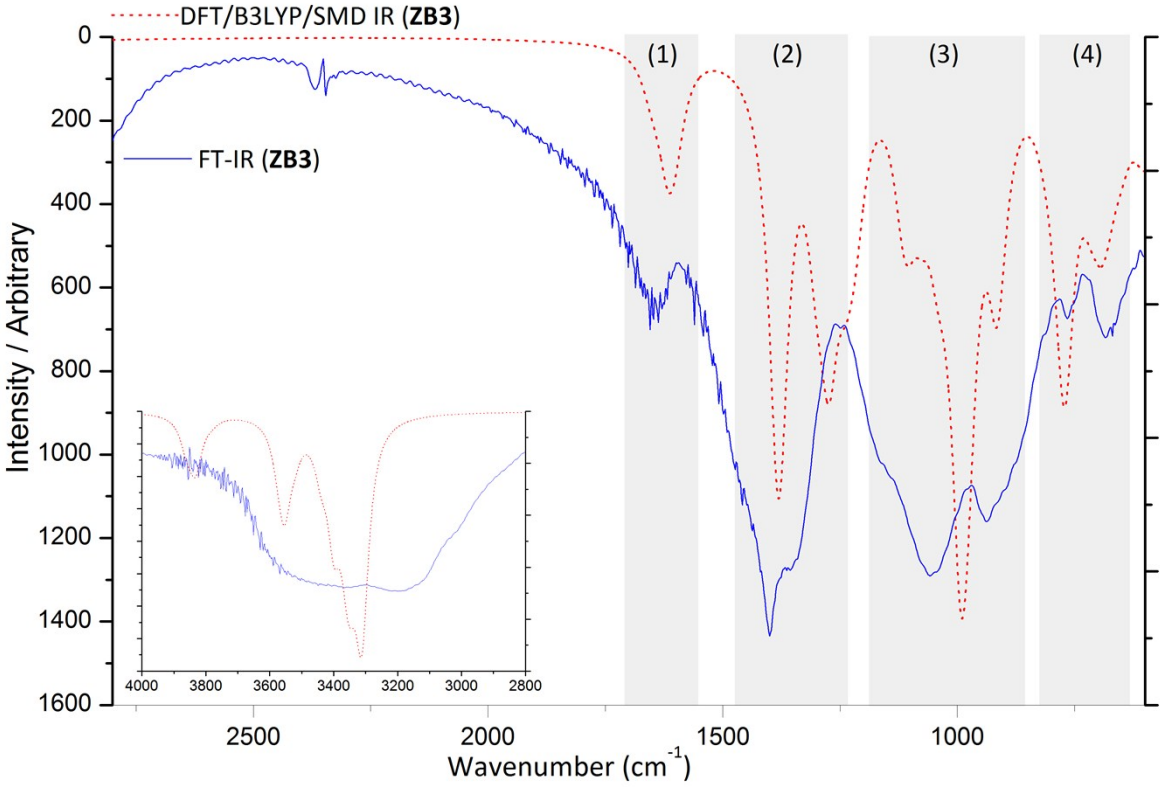


Figure S16. Experimental and DFT calculated infrared spectra for ZB3.

Table S13. Infrared normal modes assignment for ZB3.

Zone (See Fig. S16)	DFT/B3LYP (cm^{-1})	FT-IR (cm^{-1})	Assignment
1	1612	1644	σ H-O-H + σ H-N-H
2	1381	1397	ν_{as} O3-B3-O7 + ν_{as} O5-B4-O9 + σ B3-O6-H6 + σ B4-O8-H8
	1273	1349	ν_{as} O6-B3-O3 + ν_{as} O5-B4-O8
3	1115 , 1102	1156	σ H2-O2-B1 , σ H4-O4-B2
	994	1050	ρ (B4O8)-H8 + ρ (B3O6)-H6 + ρ (B2O4)-H4 + ν_{as} O2-B1-O1 + ν_{as} O4-B2-O1
	914	935	ν_s B3-$(O)_3$ + ν_s B4-$(O)_3$ + σ B1-O1-B2
4	771	765	ρ O4W-H + ν_{as} O7-B2-O1 + ν_{as} O3-B1-O1
	695	681	ρ NH_3 (N2, N3, N4)

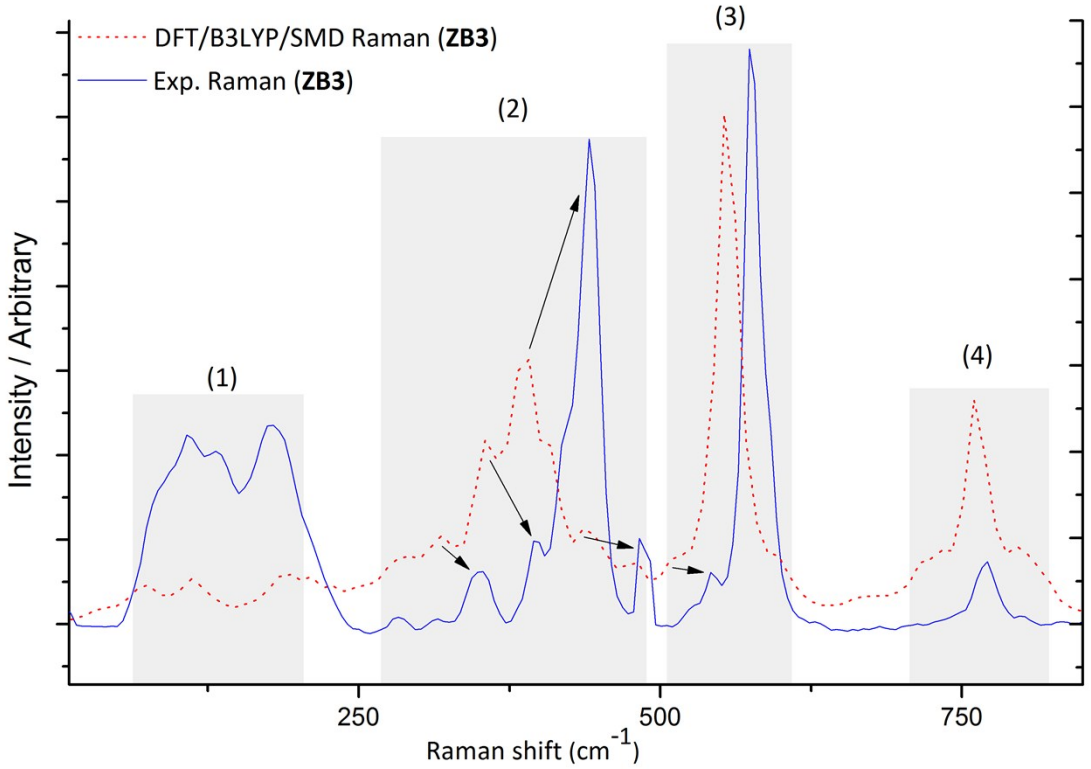


Figure S17. Experimental and DFT calculated Raman spectra for ZB3.

Table S14. Active Raman modes assignment for ZB3.

Zone (See Fig. S17)	DFT/B3LYP (cm^{-1})	Raman shift (cm^{-1})	Assignment
1	70	95	ω ($B4O_2$)-O8 + ω ($B3O_2$)-O6
	114	130	δ Zn-$(NH_3)_4$
	186	179	
2	281	281	ρ of the H bonding to OXW (X=1,3,4)
	321	350	ρ O4-H4 + τ N3-$(H)_3$
	351	394	ν Zn-N4
	388	420	ν_S Zn-$(NH_3)_4$
	438	482	σ O5-B4-O9 + σ O3-B3-O7

3	511	539	ω O9-(B2)-O7 + ω O5-(B1)-O3
	556	572	v_S B1-O + v_S B2-O
4	760	768	Symmetric ring breathing

5. Confocal Raman and SEM micrographs support information

The knowledge of the topology of the obtained solid phases is essential for future applications. Confocal Raman spectroscopy is a very powerfully technique that is independent of the crystalline state of the sample, and allows to know the distribution of different components in the sample. Figure S20 shows the results.

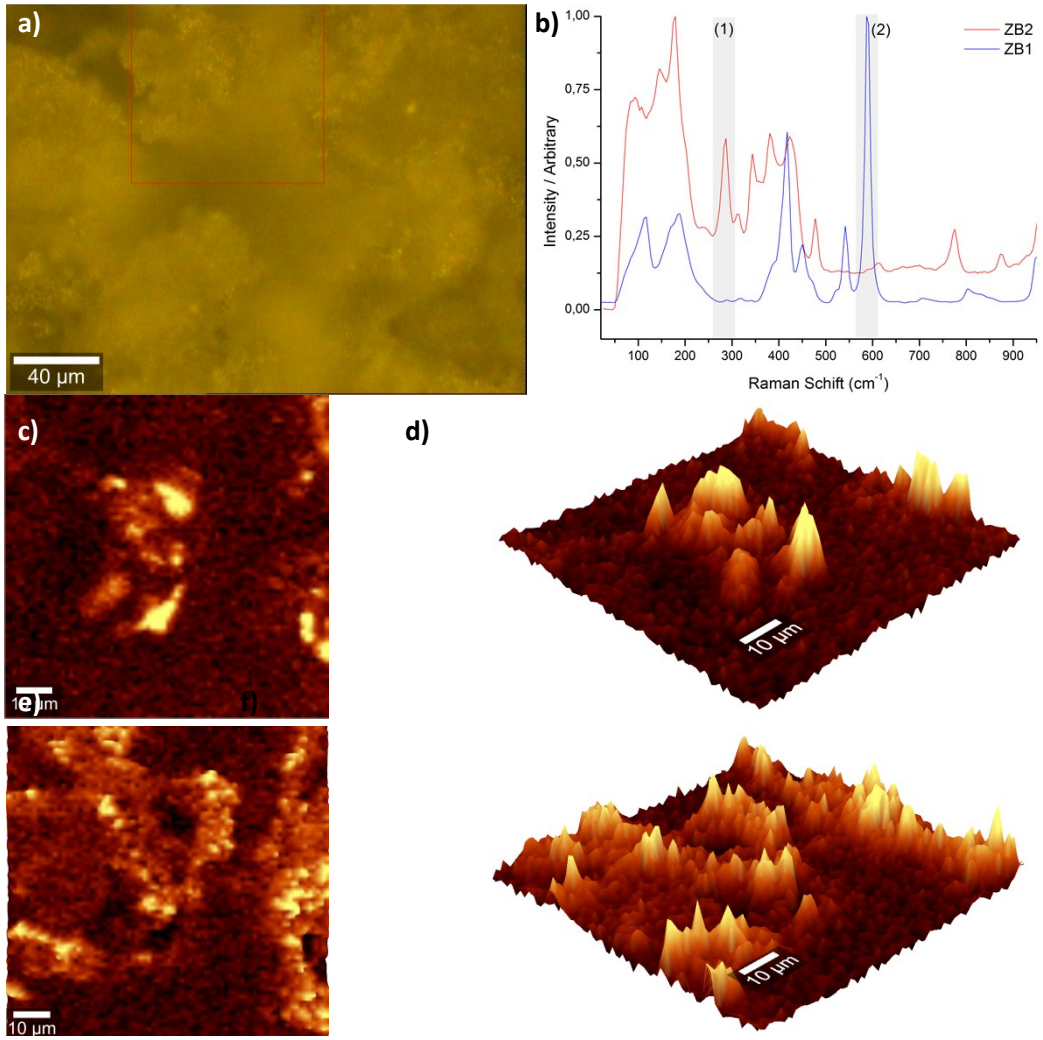


Figure S18. a) Zinc borate sample obtained in the synthesis. The red square indicate the scanned area. b) Raman bands selected to study both compounds ZB1 and ZB2 in the mixture. In c) and e) a top view of Raman intensities for ZB1 and ZB2 are shown, respectively. In d) and f), the same information is displayed as a 3D plot. The intensities of the selected bands are higher in the brighter areas.

Zones 1 and 2 in Figure S18b were selected as characteristics Raman bands of **ZB2** and **ZB1**, respectively. Figures S18c and d show the zones where the intensity counts for the characteristic band for **ZB1** is maximum. The same information is depicted for **ZB2** in Figures S18e and f. Interestingly, images c) and d) are complementary in the majority of the scanned area. The darker common zones in the images represent the area of the sample in which both solids are intimately mixed. These results suggest that although there are zones of the zinc borates composed by a mixture between **ZB1** and **ZB2**, both compounds can be found intimately mixed in the solid.

Figure S19 depicts the SEM micrographs of different zinc borates. In general, the morphology exhibited by the solids are granular, with large particle sizes (2 – 10 μm) and a homogenous distribution. In recently works, zinc borates having average

particle sizes of 2.0 through 9.0 μm are reported with granular morphology and heterogeneous distribution of particle size (M. Kılınç, G. Ö. Çakal, S. Yeşil, G. Bayram, İ. Eroğlu and S. Özkar, Journal of Crystal Growth, 2010, **312**, 3361-3366).

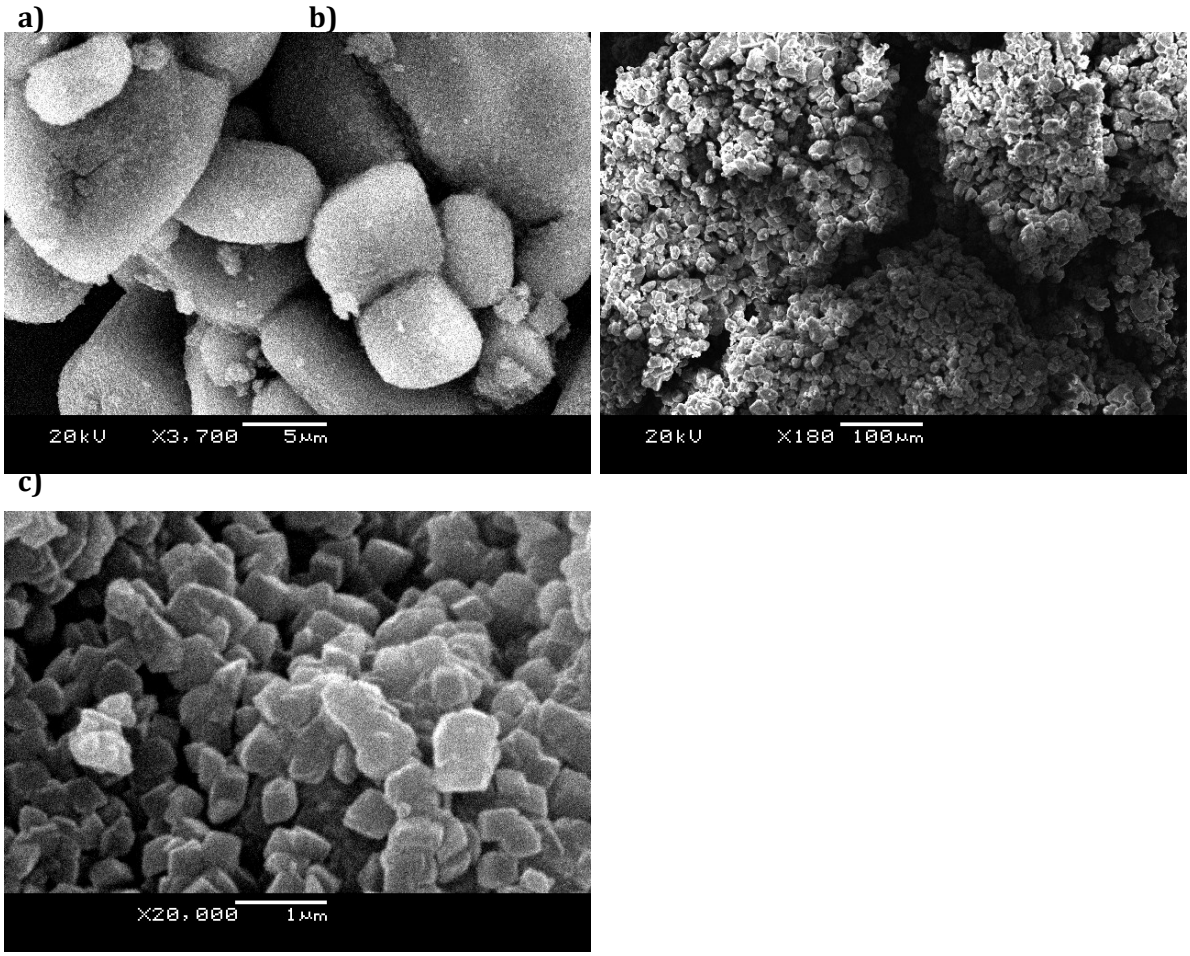


Figure S19. SEM images for different samples. a) and b) show the morphology of ZB1 obtained at 3 L in the optimum conditions. In c), the SEM image of a zinc borate sample obtained in a typical synthesis is depicted.

5. TGA analysis support information

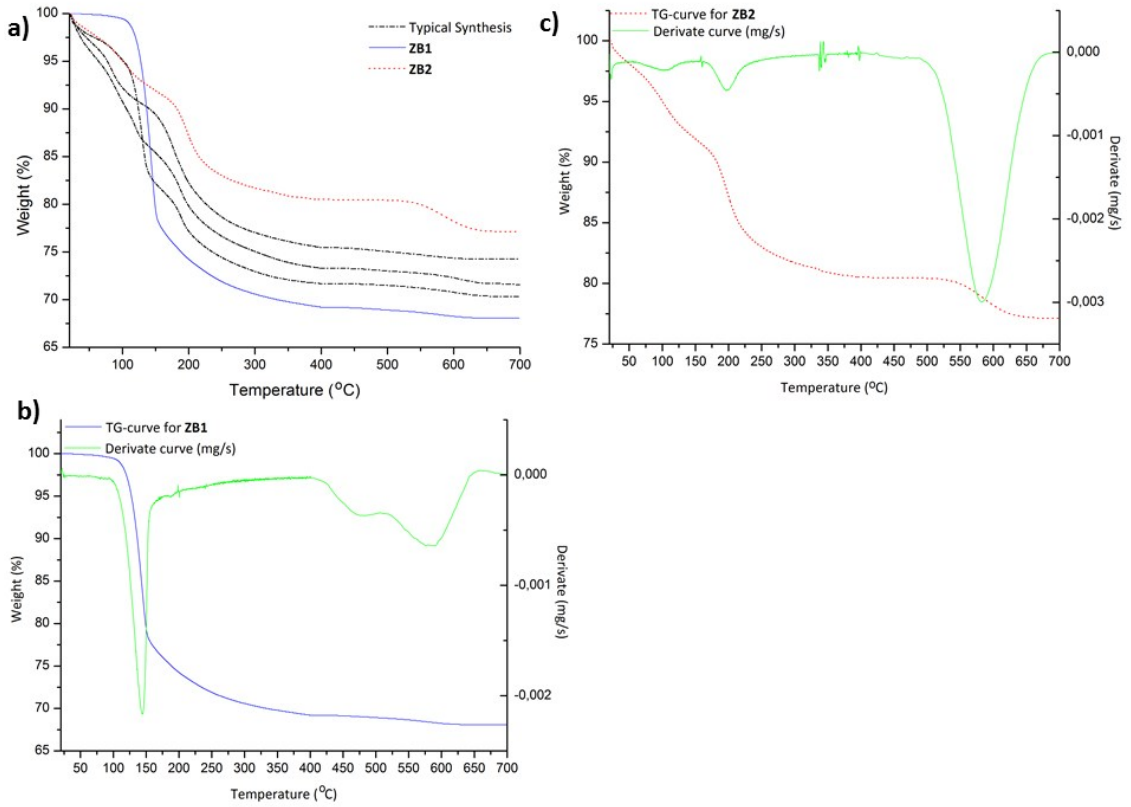


Figure S20. a) Thermogravimetric profiles for some of the zinc borates mixtures obtained in typical synthesis. The TGA and DTG curves for ZB1 (b) and ZB2 (c) are shown for comparison.

6. Powder X-ray diffraction Supplementary materials.

Table S15. Synthetic conditions tested at room temperature (V_{final} = 60 mL). The solid phases were identified by powder X-ray diffraction.

Entry	Molar ratio			Products	Yield[a] (%)	Elemental analysis[b]		
	ZnO	H_3BO_3	NH_3			%Zn	%N	%H
1	1	1	8	-	-	-	-	-
2	1	2	8	-	-	-	-	-
3	1	3	8	ZB1 + ZB2	35	23.15	6.67	3.87
4	1	4	8	ZB1 + ZB2	77	21.20	7.73	3.46
5	1	5	8	ZB1 + ZB2	61	22.55	6.79	3.41
6	1	4	1	impurities	-	81.24	0.11	0.21
7	1	4	2	impurities	-	78.58	0.87	0.65
8	1	4	3	impurities	-	80,54	0.53	0.72
9	1	4	4	ZB2 + impurities	-	29.24	2.87	2.83
10	1	4	5	ZB2 + impurities	48	26.98	4.34	2.36
11	1	4	6	ZB1 + ZB2	72	20.5	6.34	4.21
12	1	4	10	ZB1 + ZB2	78	21.92	4.68	2.54
13	1	4	12	ZB2 + impurities	52	27.54	4.71	2.57

[a] Calculated assuming **ZB1** as the only product.

[b] Theo. Elemental analysis: ZB1 (%Zn= 20.06, %N= 12.90, %H= 4.65), ZB2 (%Zn= 32.95, %N= 4.71, %H= 3.05).

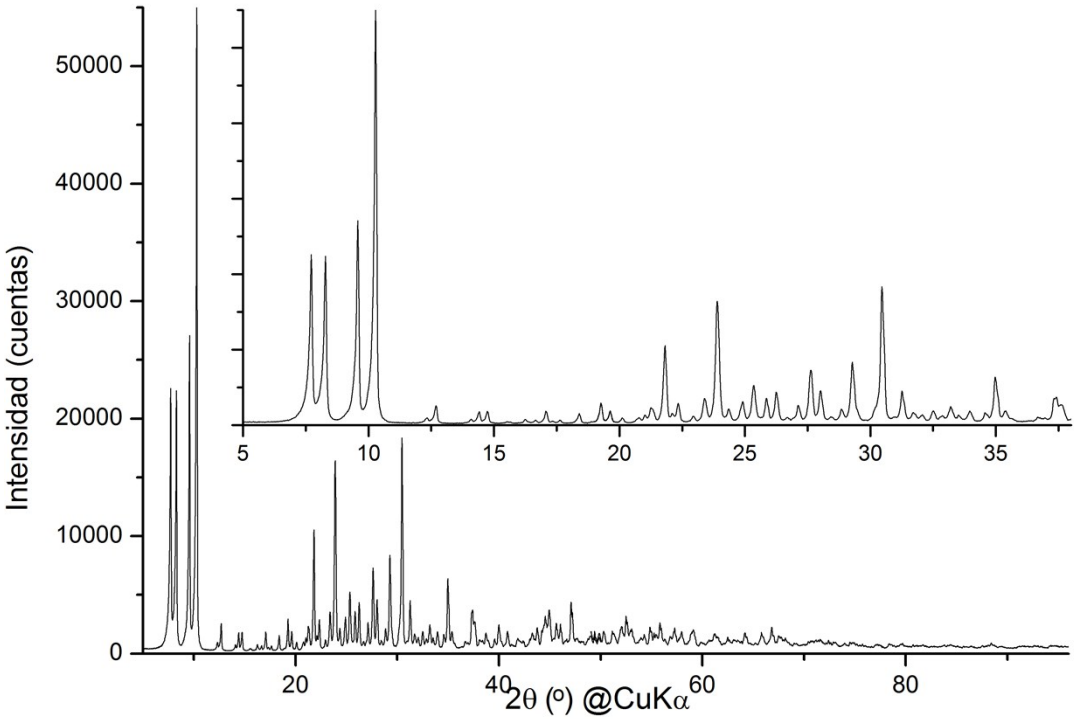


Figure S21. XRD pattern for ZB2 measured in a conventional diffractometer UltimaIV.

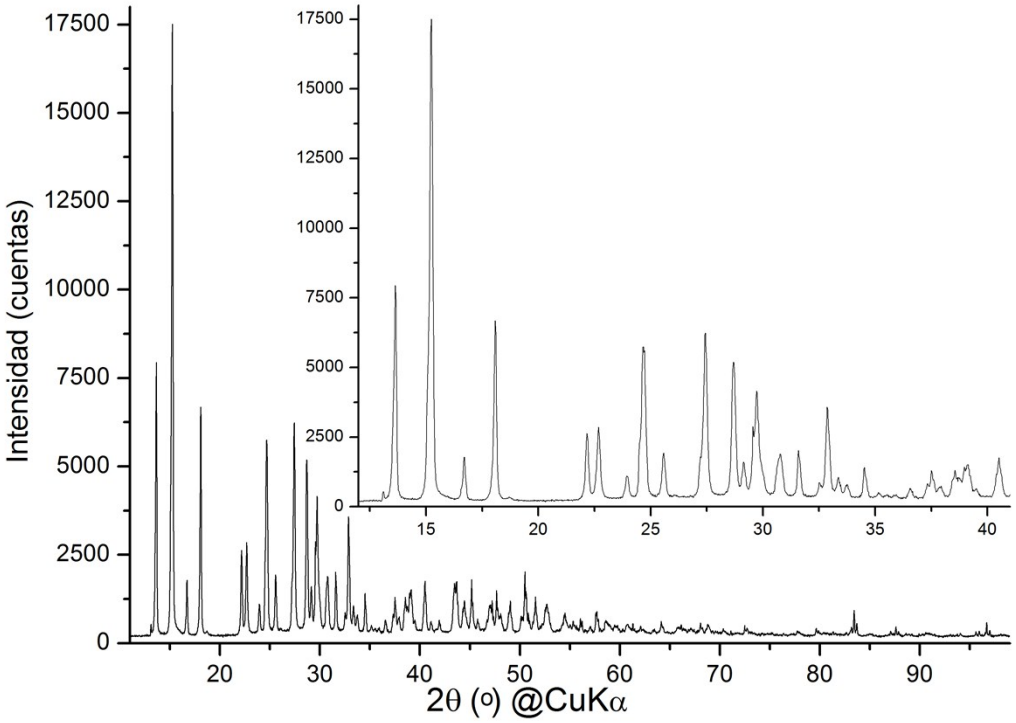


Figure 22. XRD patter for ZB1 measured in a conventional diffractometer UltimaIV.