Supporting Information

Five new rubidium borates with 0D cluster, 1D chain, 2D layer and 3D framework

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Table S1 Selected bond distances (Å) and angles (°) for compound **1**.

Rb—O1^{ii}	3.083 (5)	Na—O5^{vii}	2.380 (4)
Rb—O1^{iv}	3.128 (4)	Na—O5^{viii}	2.380 (4)
Rb—O2^{iii}	3.110 (4)	B1—O1	1.371 (8)
Rb—O3	2.916 (4)	B1—O2	1.370 (7)
Rb—O3^{i}	2.976 (4)	B1—O3	1.369 (8)
Rb—O5	3.009 (4)	B2—O2^{ix}	1.489 (7)
Rb—O5^{v}	3.160 (4)	B2—O3	1.494 (7)
Na—O5	2.380 (4)	B2—O4	1.453 (7)
Na—O5^{i}	2.380 (4)	B2—O5	1.453 (7)
Na—O5^{v}	2.380 (4)	O1—H1	0.8434
Na—O5^{vi}	2.380 (4)	O5—H5	0.8458
O3—B1—O2	122.6 (5)	O5—B2—O4	111.2 (5)
O3—B1—O1	118.4 (5)	O5—B2—O2^{ix}	109.6 (4)
O2—B1—O1	119.0 (5)	O4—B2—O2^{ix}	110.0 (5)
O2^{ix}—B2—O3	108.1 (5)	O5—B2—O3	108.1 (4)
O4—B2—O3	109.7 (4)		

Symmetry codes: (i) $x - y, -y, -z + 1$; (ii) $-x + 1, -x + y + 1, -z + 1$; (iii) $-y + 1/3, x - y - 1/3, z - 1/3$; (iv) $-x + y + 1, -x + 1, z$; (v) $y, x, -z + 1$; (vi) $-x, -x + y, -z + 1$; (vii) $-x + y, -x, z$; (viii) $-y, x - y, z$; (ix) $-x + 2/3, -x + y + 1/3, -z + 4/3$.

Table S2 Selected bond distances (Å) and angles (°) for compound **2**.

Rb1—O1^{iii}	3.086 (3)	B1—O1	1.376 (5)
Rb1—O2	2.887 (2)	B1—O2	1.337 (4)
Rb1—O3^{i}	3.097 (2)	B1—O3	1.376 (4)
Rb1—O4^{ii}	2.930 (2)	B2—O2	1.464 (4)
Rb1—O6^{i}	2.895 (3)	B2—O4	1.453 (4)
Rb1—O7^{ii}	3.242 (2)	B2—O5	1.486 (4)
Rb1—O9^{iv}	3.183 (3)	B2—O11^{ix}	1.474 (4)
Rb1—O10^{iv}	2.986 (2)	B3—O3	1.401 (4)
Rb1—O11^{iii}	2.941 (2)	B3—O5	1.350 (5)
Rb2—O1^{i}	3.021 (3)	B3—O6	1.345 (4)
Rb2—O3^{iii}	3.326 (2)	B4—O4	1.350 (4)
Rb2—O4^{viii}	3.018 (2)	B4—O7	1.360 (4)
Rb2—O5	2.934 (2)	B4—O8	1.387 (4)
Rb2—O6^{iii}	3.316 (3)	B5—O6^{vii}	1.475 (4)

Rb2—O7^{viii}	3.328 (2)	B5—O7	1.483 (4)
Rb2—O9^{vi}	2.928 (2)	B5—O9	1.444 (4)
Rb2—O10^{vii}	3.008 (2)	B5—O10	1.465 (4)
Rb2—O11^{iii}	3.062 (2)	B6—O8	1.402 (4)
O1—H1	0.796 (19)	B6—O10	1.363 (4)
O9—H9	0.78 (4)	B6—O11	1.338 (4)
O2—B1—O1	121.4 (3)	O4—B4—O7	117.1 (3)
O2—B1—O3	122.7 (3)	O4—B4—O8	123.0 (3)
O1—B1—O3	115.9 (3)	O7—B4—O8	119.8 (3)
O4—B2—O5	110.1 (3)	O9—B5—O10	111.6 (3)
O2—B2—O5	111.4 (3)	O9—B5—O6^{vii}	109.1 (3)
O11^{iii}—B2—O5	107.1 (3)	O10—B5—O6^{vii}	111.9 (3)
O4—B2—O2	110.8 (3)	O9—B5—O7	105.6 (3)
O4—B2—O11^{iii}	110.3 (3)	O10—B5—O7	111.3 (3)
O2—B2—O11^{iii}	107.0 (3)	O6^{vii}—B5—O7	107.1 (3)
O6—B3—O5	125.3 (3)	O11—B6—O10	125.2 (3)
O6—B3—O3	114.0 (3)	O11—B6—O8	115.6 (3)
O5—B3—O3	120.7 (3)	O10—B6—O8	119.3 (3)

Symmetry codes: (i) $-x + 1, y + 1/2, -z + 1/2$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $x, y + 1, z$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $x - 1, -y + 3/2, z - 1/2$; (vi) $x, -y + 3/2, z - 1/2$; (vii) $-x + 2, -y + 1, -z + 1$; (viii) $-x + 2, -y + 2, -z + 1$; (ix) $x, y - 1, z$.

Table S3 Selected bond distances (Å) and angles (°) for compound **3**.

Rb—O1	2.853 (6)	B1—O1	1.451 (10)
Rb—O2^{ii}	2.988 (5)	B1—O2	1.467 (10)
Rb—O3^{iii}	3.318 (5)	B1—O3	1.487 (10)
Rb—O4^{v}	3.055 (5)	B1—O8^{x}	1.464 (10)
Rb—O6^{iii}	3.020 (6)	B2—O2	1.340 (11)
Rb—O7^{i}	2.887 (5)	B2—O4	1.345 (11)
Rb—O7^{iii}	3.357 (6)	B2—O5	1.402 (10)
Rb—O8^{v}	3.309 (6)	B3—O3	1.356 (11)
Rb—O9^{v}	3.302 (6)	B3—O5	1.390 (10)
Rb—O11^{iv}	3.030 (7)	B3—O6	1.347 (10)
Ba—O1^{iv}	3.085 (6)	B4—O4^{ix}	1.463 (10)
Ba—O2^{iv}	2.914 (5)	B4—O6	1.446 (11)
Ba—O3^{viii}	3.230 (5)	B4—O7	1.497 (10)

Ba—O4^{vii}	2.837 (6)	B4—O10	1.466 (11)
Ba—O6^{viii}	2.864 (6)	B5—O7	1.342 (11)
Ba—O8^{vi}	2.818 (6)	B5—O8	1.341 (11)
Ba—O9^{vi}	3.000 (6)	B5—O9	1.403 (11)
Ba—O10	2.804 (5)	B6—O9	1.365 (11)
Ba—O11^{vii}	3.006 (6)	B6—O10	1.347 (11)
O1—H1	0.8146	B6—O11	1.374 (11)
O11—H11	0.8190		
O1—B1—O8^{x}	109.2 (7)	O6—B4—O4^{vii}	111.0 (7)
O1—B1—O2	111.7 (6)	O6—B4—O10	111.1 (7)
O8^{x}—B1—O2	112.6 (6)	O4^{vii}—B4—O10	106.8 (7)
O1—B1—O3	105.2 (6)	O6—B4—O7	109.7 (7)
O8^{x}—B1—O3	106.8 (6)	O4^{vii}—B4—O7	107.4 (6)
O2—B1—O3	111.1 (6)	O10—B4—O7	110.9 (7)
O2—B2—O4	125.4 (7)	O8—B5—O7	125.6 (8)
O2—B2—O5	119.9 (7)	O8—B5—O9	113.3 (8)
O4—B2—O5	114.7 (8)	O7—B5—O9	121.1 (8)
O6—B3—O3	117.5 (7)	O10—B6—O9	123.0 (8)
O6—B3—O5	123.0 (8)	O10—B6—O11	120.5 (8)
O3—B3—O5	119.5 (7)	O9—B6—O11	116.4 (7)

Symmetry codes: (i) *x*, −*y* + 1/2, *z* − 1/2; (ii) −*x*, *y* − 1/2, −*z* + 1/2; (iii) −*x*, *y* + 1/2, −*z* + 1/2; (iv) −*x* + 1, −*y* + 1, −*z* + 1; (v) *x*, −*y* + 3/2, *z* − 1/2; (vi) −*x* + 1, *y* − 1/2, −*z* + 3/2; (vii) *x*, *y* − 1, *z*; (viii) −*x* + 1, −*y*, −*z* + 1; (ix) *x*, *y* + 1, *z*; (x) −*x*, −*y* + 1, −*z* + 1.

Table S4 Selected bond distances (Å) and angles (°) for compound **4**.

Rb1—O1	3.141 (2)	B1—O1	1.363 (4)
Rb1—O2	2.909 (2)	B1—O2	1.374 (5)
Rb1—O3^{vii}	2.889 (3)	B1—O3	1.361 (4)
Rb1—O5^{ix}	3.380 (3)	B2—O1^{xi}	1.463 (4)
Rb1—O6^{i}	2.736 (2)	B2—O2	1.467 (4)
Rb1—O6^{iii}	2.841 (2)	B2—O4	1.492 (5)
Rb1—O8^{ii}	3.419 (3)	B2—O5	1.457 (5)
Rb1—O9^{viii}	3.056 (3)	B3—O3	1.483 (4)
Rb1—O9^{x}	3.479 (3)	B3—O5	1.431 (4)
Rb2—O1^{v}	3.304 (2)	B3—O6	1.496 (5)
Rb2—O2^{v}	2.919 (2)	B3—O7	1.514 (4)
Rb2—O3^{vi}	2.957 (3)	B4—O4^{i}	1.340 (5)
Rb2—O4	2.807 (3)	B4—O6	1.355 (5)
Rb2—O5	3.258 (3)	B4—O8	1.408 (5)
Rb2—O7	3.067 (3)	B5—O7	1.347 (5)
Rb2—O7^{iv}	2.895 (2)	B5—O8	1.391 (5)
Rb2—O8^{i}	2.939 (3)	B5—O9	1.358 (5)
Rb2—O9	3.428 (3)	O9—H9	0.818 (14)
O3—B1—O1	124.8 (3)	O3—B3—O7	106.7 (3)
O3—B1—O2	121.3 (3)	O5—B3—O7	112.6 (3)
O1—B1—O2	113.9 (3)	O6—B3—O7	106.3 (3)
O1^{xii}—B2—O4	107.9 (3)	O4^{i}—B4—O6	125.6 (3)
O1^{xii}—B2—O2	110.4 (3)	O4^{i}—B4—O8	115.5 (3)
O2—B2—O4	109.0 (3)	O6—B4—O8	118.9 (3)
O5—B2—O1^{xii}	110.9 (3)	O7—B5—O9	123.8 (3)
O5—B2—O2	110.8 (3)	O7—B5—O8	121.5 (3)
O5—B2—O4	107.7 (3)	O9—B5—O8	114.6 (3)
O3—B3—O6	108.6 (3)		

Symmetry codes: (i) $-x + 3/2, y, z - 1/2$; (ii) $-x + 3/2, y - 1, z - 1/2$; (iii) $-x + 1, -y + 2, z - 1/2$; (iv) $x - 1/2, -y + 1, z$; (v) $x, y - 1, z$; (vi) $x + 1/2, -y + 1, z$; (vii) $-x + 1, -y + 2, z + 1/2$; (viii) $-x + 3/2, y + 1, z + 1/2$; (ix) $-x + 3/2, y, z + 1/2$; (x) $-x + 1, -y + 1, z + 1/2$; (xi) $x - 1/2, -y + 2, z$; (xii) $x + 1/2, -y + 2, z$.

Table S5 Selected bond distances (Å) and angles (°) for compound **5**.

Na—O1^{i}	2.4093 (12)	B1—O3	1.361 (2)
Na—O3^{i}	2.3203 (14)	B2—O1	1.4571 (19)
Rb—O1	3.5750 (12)	B2—O2^{ii}	1.4466 (19)
Rb—O2^{iii}	2.9149 (11)	B2—O3^{iv}	1.452 (2)
B1—O1	1.378 (2)	B2—O4	1.5313 (16)
B1—O2	1.356 (2)		
O2—B1—O3	123.49 (15)	O2^{v}—B2—O3^{vi}	112.63 (13)
O2—B1—O1	122.20 (14)	O2^{v}—B2—O1	109.59 (13)
O3—B1—O1	114.31 (16)	O3^{vi}—B2—O1	110.55 (12)
O1—B2—O4	107.88 (12)	O3^{vi}—B2—O4	107.25 (13)
O2^{v}—B2—O4	108.79 (11)		

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-z + 1/2, -x + 1, y - 1/2$; (iii) $-x + 1/2, -y + 1, z - 1/2$; (iv) $y - 1/2, z, -x + 1/2$; (v) $-y + 1, z + 1/2, -x + 1/2$; (vi) $-z + 1/2, x + 1/2, y$.

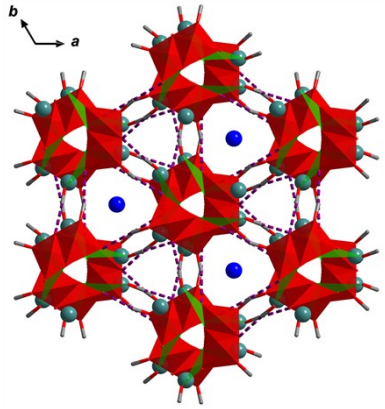

Fig. S1 View of the supramolecular 2D structure of compound **1** along the *c* axis. Color code for atom: Na: blue, Rb: teal. Color code for polyhedra: BO_4: red, BO_3: green, similarly hereinafter.

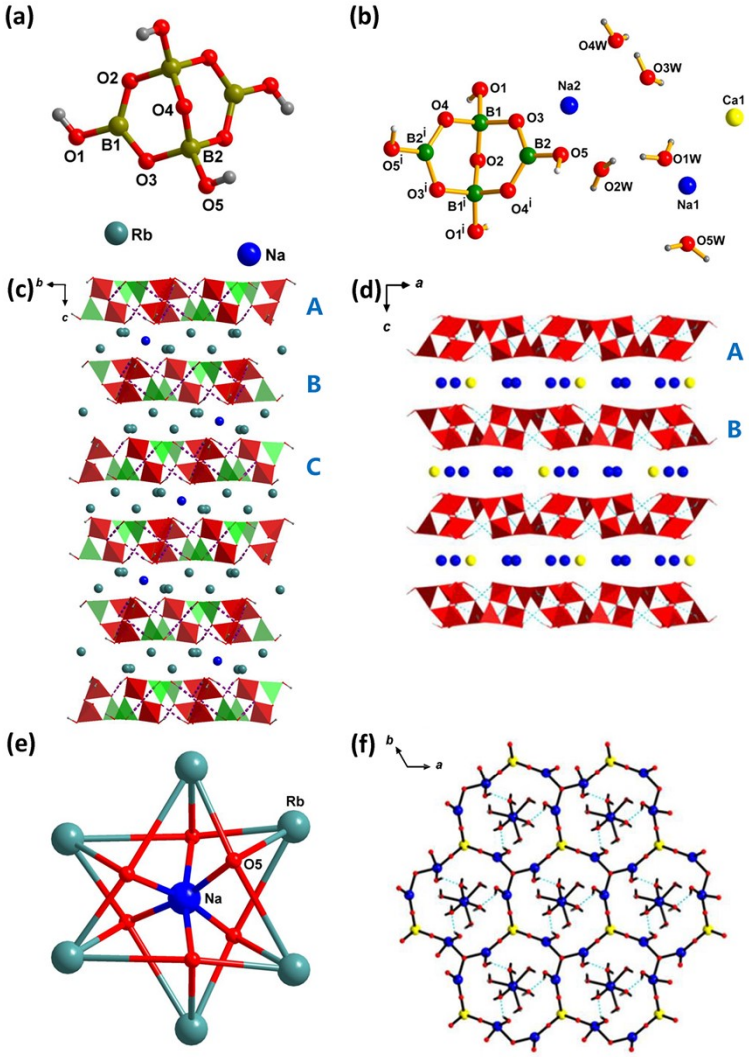

Fig. S2 Structure of compounds **1** (a) and **1a** (b). Symmetry codes: (i) $1 + x - y$, $2 - y$, $1 - z$. The arrangement of supramolecular structure of compounds **1** (c) and **1a** (d). View of the 0D Na–O–Rb cluster of **1** (e) and the 2D Na–O–Ca layer of **1a** (f).

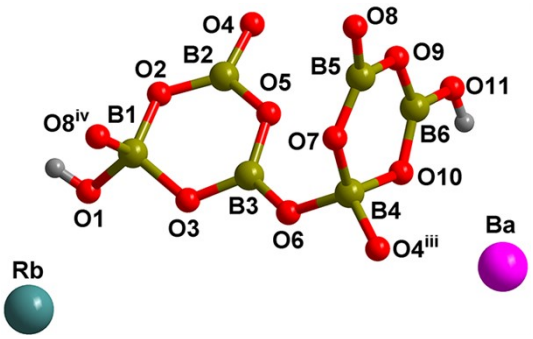

Fig. S3 Asymmetric unit of compound **3**. Symmetry codes: (i) $x, -1 + y, z$; (ii) $-x, 1 - y, 1 - z$.

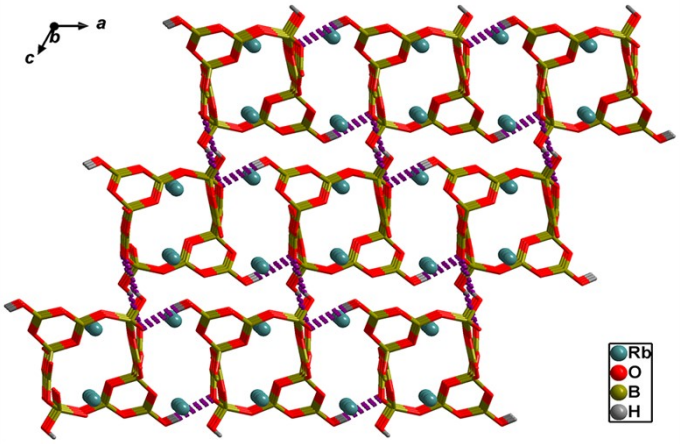

Fig. S4 3D supramolecular structure of compound **2** along the *b* axis connected by O9–H9···O7 hydrogen bonds (2.354 Å, 3.041 Å, 148º, dashed lines) with the charge balancing Rb^+ ions.

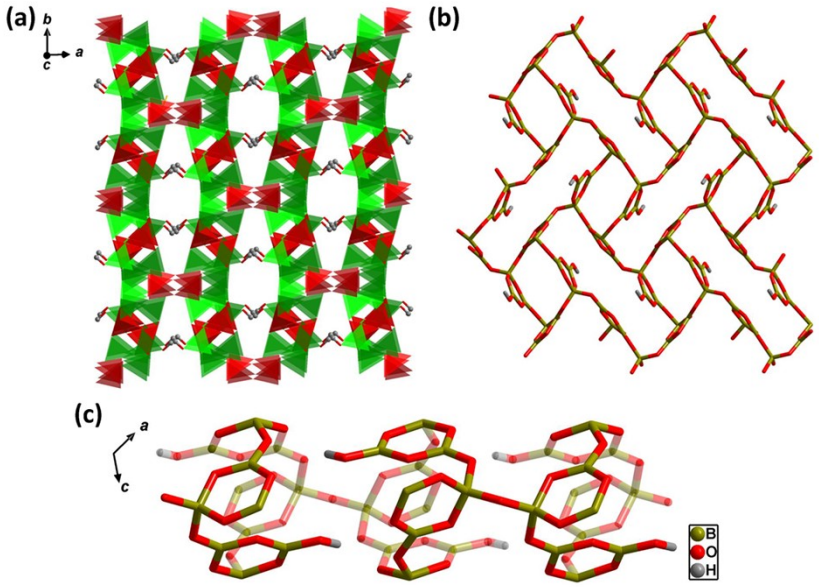

Fig. S5 (a) 3D framework of compound **2a** along the *c* axis. (b) 2D layer of **2a** assuming O11 atoms are protonated. (c) 1D chain of **2a** assuming O6 atoms are protonated.

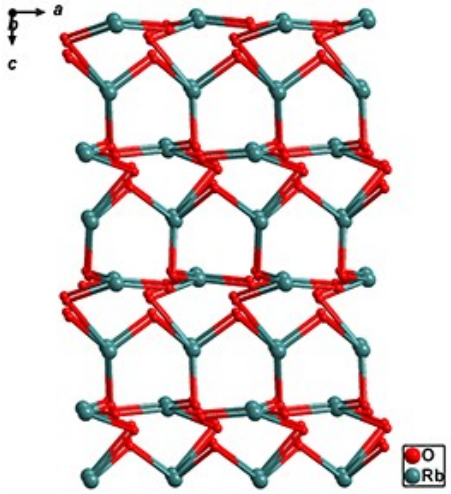

Fig. S6 View of the Rb–O framework of **4** along the *b* axis.

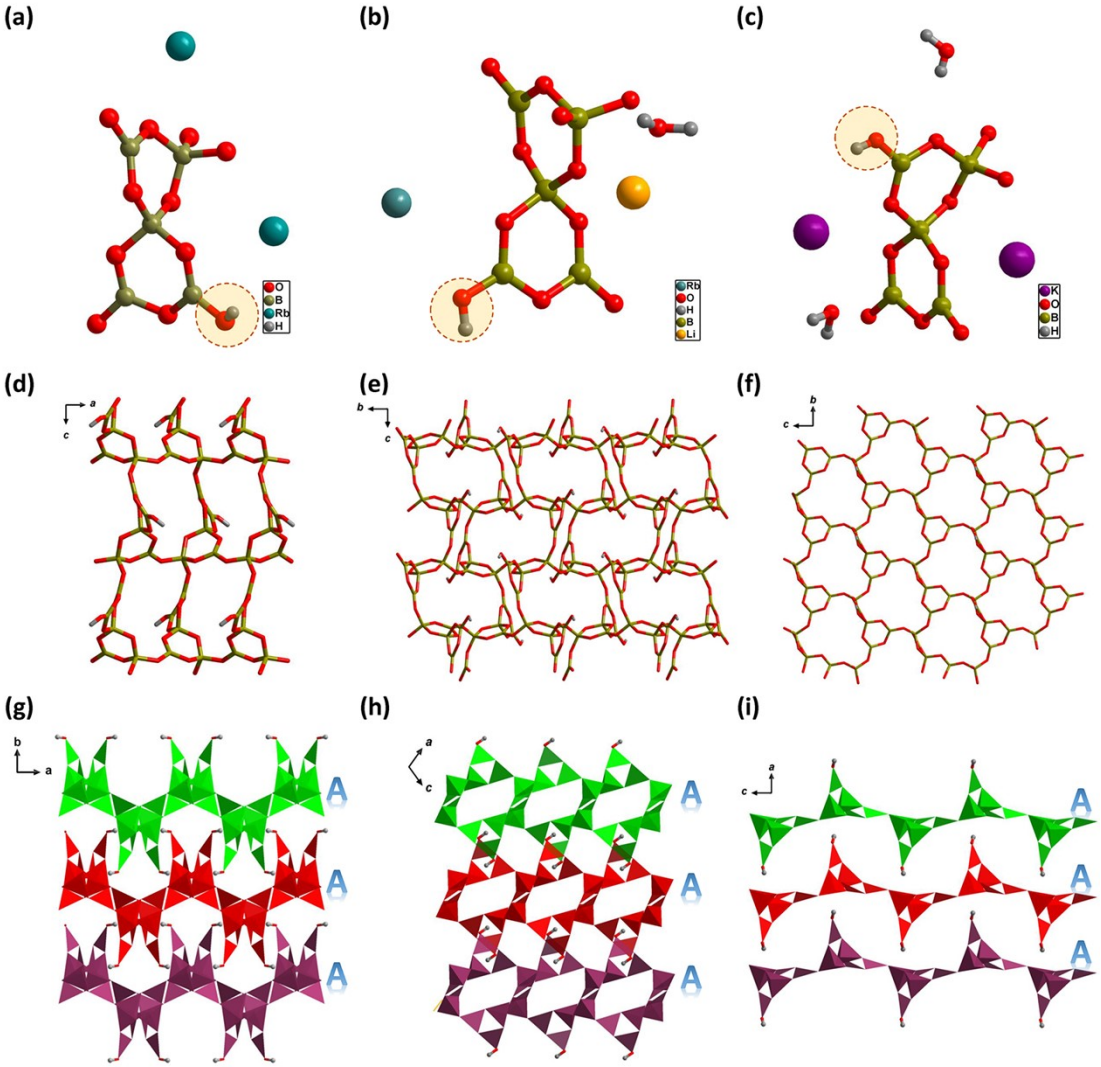

Fig. S7 Asymmetric unit of compounds **4** (a), **4a** (b) and **4b** (c). The 2D layers with 3- and 9-MR in **4**(d), 8- and 10-MR in **4a**(e), 3- and 9-MR in **4b**(f). The arrangements of **4** (g), **4a** (h) and **4b** (i).

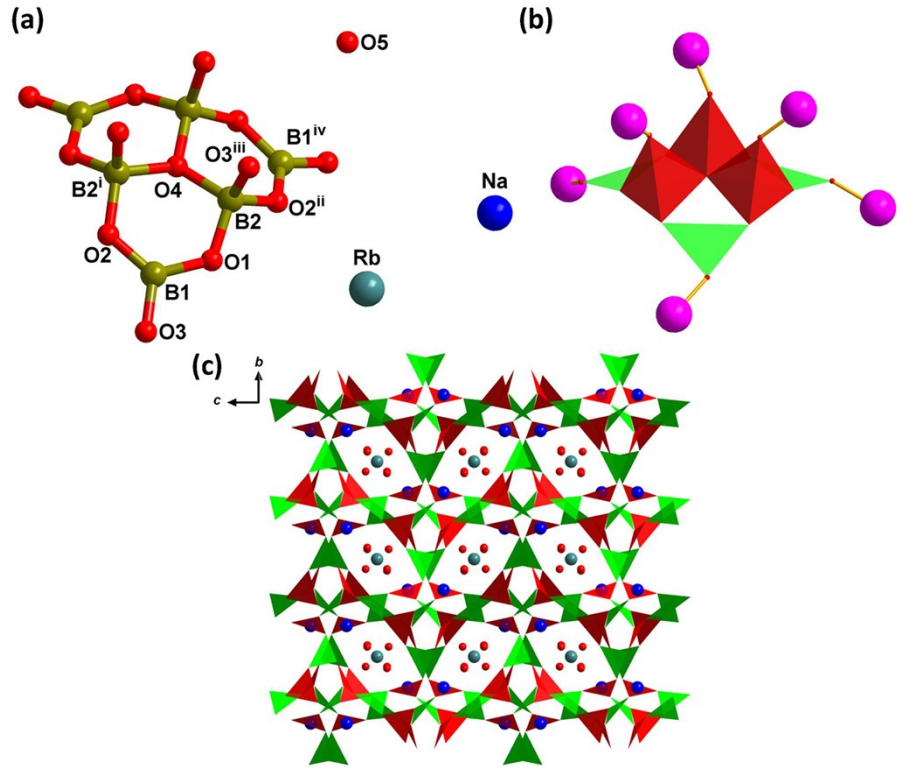

Fig. S8 (a) View of the structure of compound **5**, symmetry codes: (i) 0.5 − *z*, 1 − *x*, −0.5 + *y*; (ii) 1 − *y*, 0.5 + *z*, 0.5 − *x*; (iii) 0.5 − *z*, 0.5 + *x*, *y*; (iv) 1 − *y*, 0.5 + *z*, 0.5 − *x*. (b) View of the linkage of $\{B_6O_{13}\}$ cluster units, in which the $\{B_6O_{13}\}$ clusters are shown as pink nodes. (c) 3D framework viewed along the *a* axis.

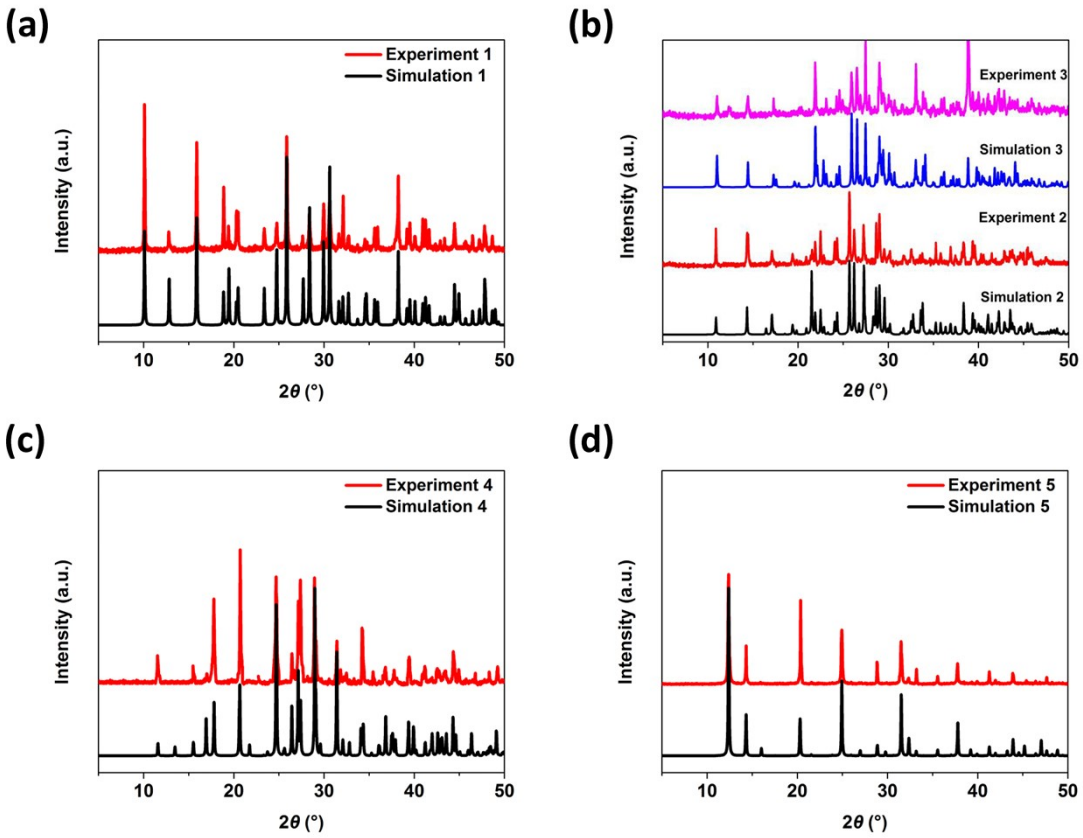

Fig. S9 PXRD patterns show the comparison between the experimental value and calculated ones for compounds **1**(a), **2**–**3**(b), **4**(c) and **5**(d).

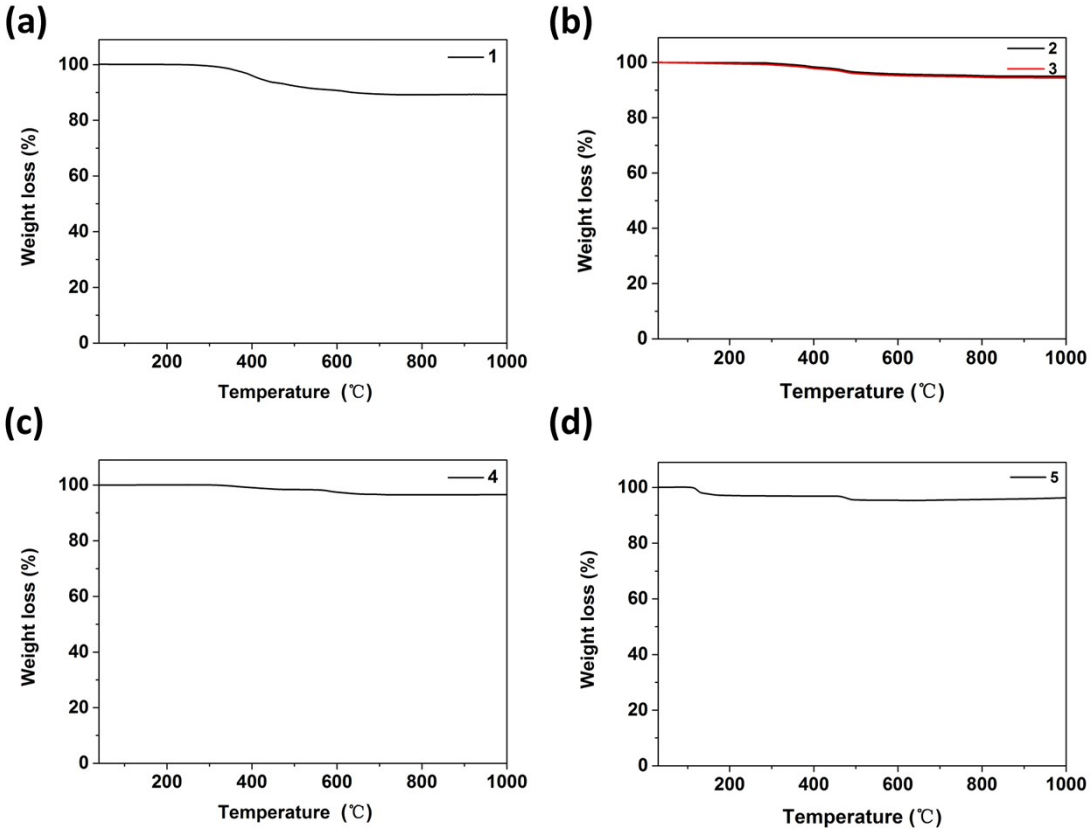

Fig. S10 TG curves for compounds **1**(a), **2**–**3**(b), **4**(c) and **5**(d).

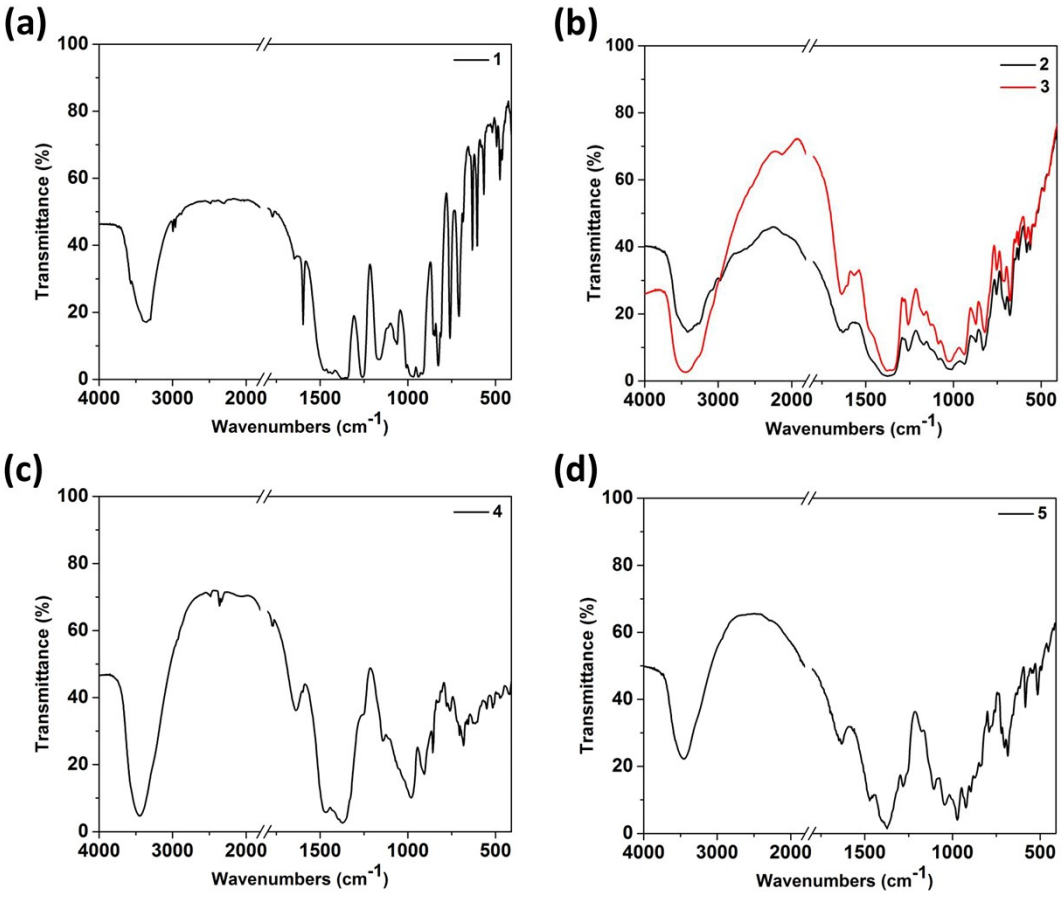

Fig. S11 IR spectra for compounds **1**(a), **2**–**3**(b), **4**(c) and **5**(d).

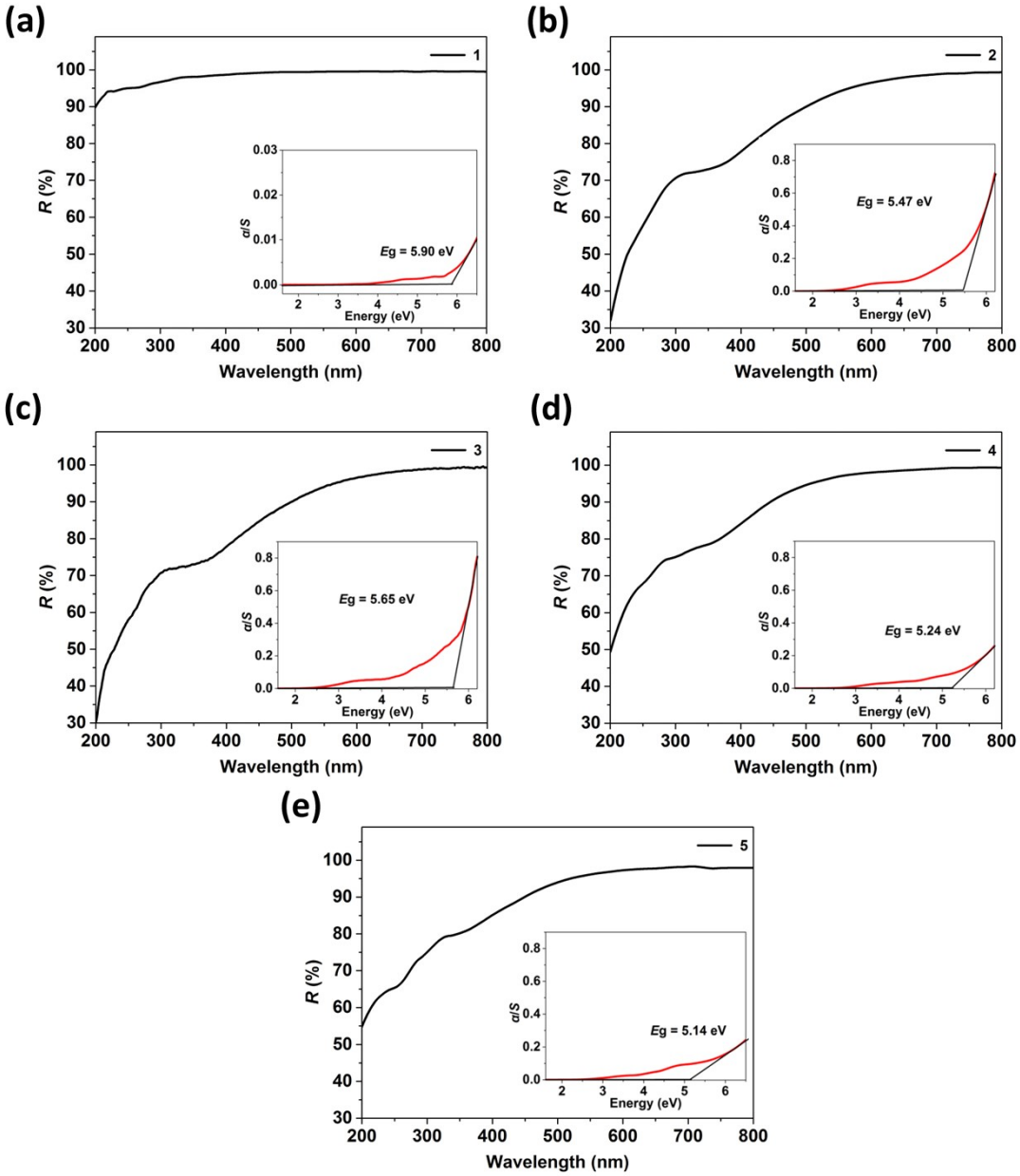

Fig. S12 UV/Vis diffuse reflectance spectra of compounds **1**(a), **2**(b), **3**(c), **4**(d) and **5**(e). Inset: plots of α/S *vs*. *E*.

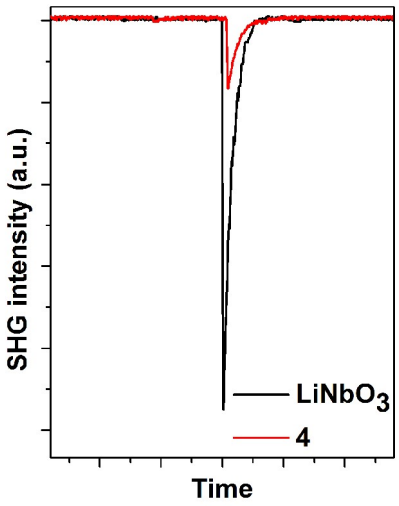

Fig. S13 Oscilloscope traces of SHG signals for compounds **4** and $LiNbO_3$ in the same particle size of 150–212 μm.

Table S6 The direction and magnitude (in Debye) of the polyhedral dipole moments for compound **1**

Specie	*a*	*b*	*c*	Magnitude
Compound **1**				
NaO_6	0 × 2	0 × 2	±0.02	0.02
	0 × 4	0 × 4	0 × 4	0
	0	**0**	**0**	
RbO_7	–4.84 × 3	4.75 × 3	–2.82 × 3	7.35
	–4.75 × 3	–9.59 × 3	–2.82 × 3	11.11
	–9.59 × 3	–4.75 × 3	2.82 × 3	11.11
	4.84 × 3	9.59 × 3	2.82 × 3	11.11
	4.75 × 3	–4.84 × 3	2.82 × 3	7.35
	9.59 × 3	4.84 × 3	–2.82 × 3	11.11
	0	**0**	**0**	
BO_3	–0.36 × 2	0.45 × 2	–0.29 × 2	0.65
	0.45 × 2	–0.09 × 2	–0.29 × 2	0.54
	–0.09 × 2	–0.36 × 2	–0.29 × 2	0.47
	–0.45 × 2	0.36 × 2	0.29 × 2	0.65
	0.36 × 2	0.09 × 2	0.29 × 2	0.47
	0.09 × 2	–0.45 × 2	0.29 × 2	0.54
	0.09	–0.45	0.33	0.56
	0.36	0.09	0.33	0.50
	–0.45	0.36	0.33	0.66
	–0.36	0.45	–0.33	0.66
	0.45	–0.09	–0.33	0.56
	–0.09	–0.36	–0.33	0.50
	0	**0**	**0**	
Unit Cell	**0**	**0**	**0**	**0**