Supporting Information

Two Deep-Ultraviolet Nonlinear Optical Alkaline-Earth Metal Borates Based on Different Types of Oxoboron Clusters

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Table S1. Hydrogen bond lengths (Å) and angles (°) compounds **1** and **2**.

Interaction	H…A	D…A	Angle	Symmetry codes
Compound 1				
O1W-H1WA...O23	1.952	2.846	160.57	[-*x*+2, *y*-1/2, -*z*+1]
O1W-H1WB...O20	1.711	2.638	174.89	[-*x*+2, *y*-1/2, -*z*]
O1-H1A...O13	2.148	2.958	169.36	
O2-H2A...O3	1.822	2.629	167.61	[-*x*+1, *y*+1/2, -*z*]
O3-H3A...O5	1.922	2.709	160.44	[-*x*+2, *y*-1/2, -*z*+1]
O20-H20A...O16	1.978	2.767	161.23	[-*x*+2, *y*+1/2, -*z*+1]
O23-H23A...O1W	2.165	2.846	136.93	[-*x*+2, *y*+1/2, -*z*+1]
Compound 2				
O2-H2A...O12	1.955	2.727	156.48	[*x*-1/2, -*y*-1, *z*-1/2]
O2-H2A...O2W	2.303	2.837	123.24	[-*x*-1, *y*, *z*-1]
O8-H8A...O1W	1.971	2.649	140.25	[-*x*-1, *y*-1, *z*-1]
O11-H11A...O4	2.409	3.111	144.11	
O13-H13A...O10	2.485	3.262	158.51	[*x*, *y*, *z*+1]
O13-H13A...O3	2.617	3.084	117.57	[*x*, *y*, *z*+1]
O1W-H1WA...O7	2.57	3.067	118.99	[-*x*-1/2, -*y*, *z*+1/2]
O1W-H1WB...O8	1.869	2.649	151.79	[*x*, *y*+1, *z*+1]
O2W-H2WA...O5	2.499	3.247	147.36	[*x*-1/2, -*y*-1, *z*-1/2]

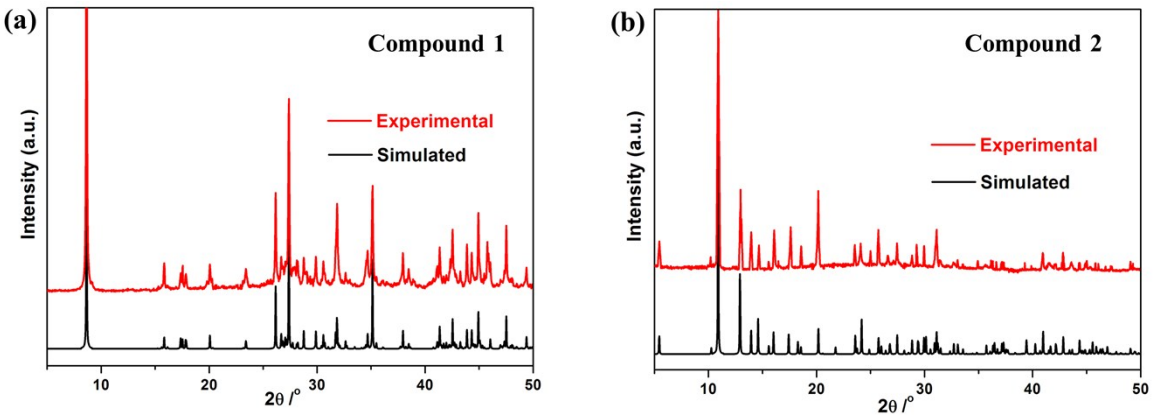

Figure S1. Experimental and simulated PXRD patterns of compounds **1** (a) and **2** (b).

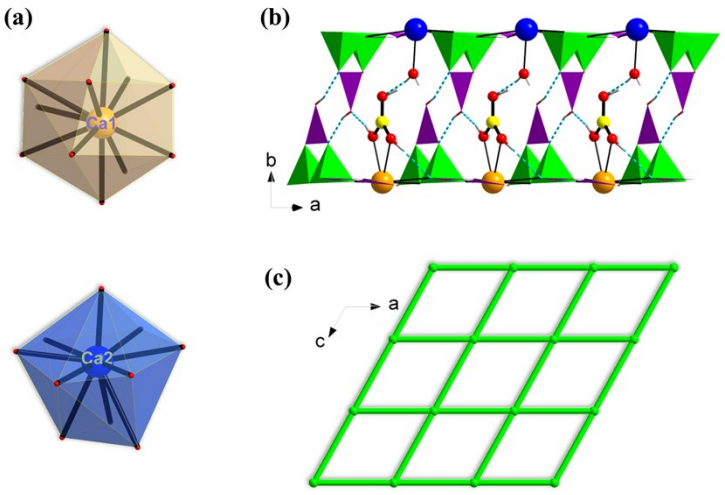

Figure S2. (a) View of the coordination environments of Ca atoms in **1**. (b) View of the linkage of the double-layer through Ca-O and H-bonds. (c) View of *spl* topology network of A- and B-layer.

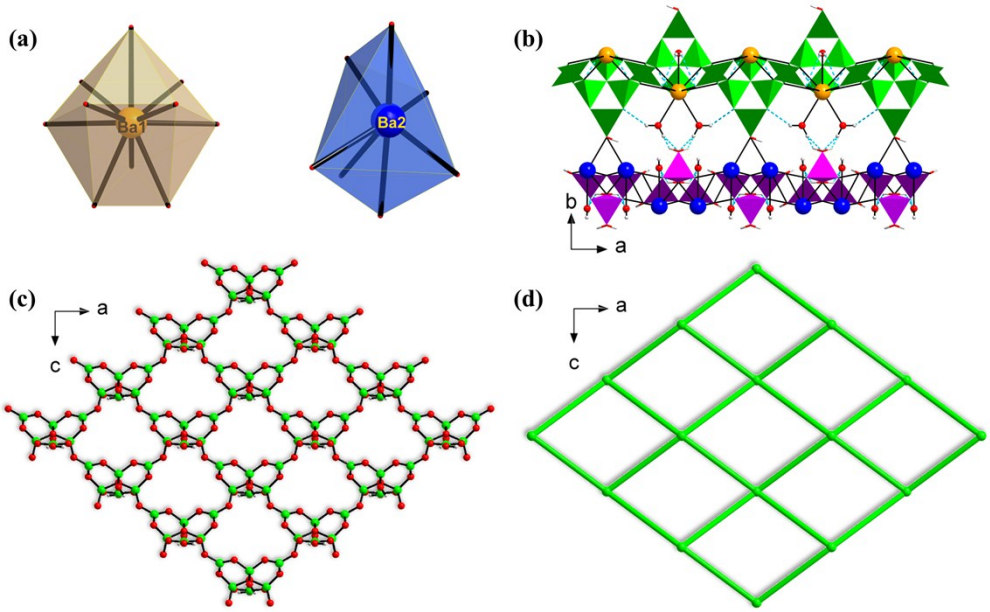

Figure S3. (a) View of the coordination environments of Ba atoms in **2**. (b) View of the linkage of Ba1-B_6-layer and Ba2-B_3-layer through Ba-O and H-bonds. (c) View of B_6-layer along [010] direction. (d) View of *spl* topology network of B_6-layer.

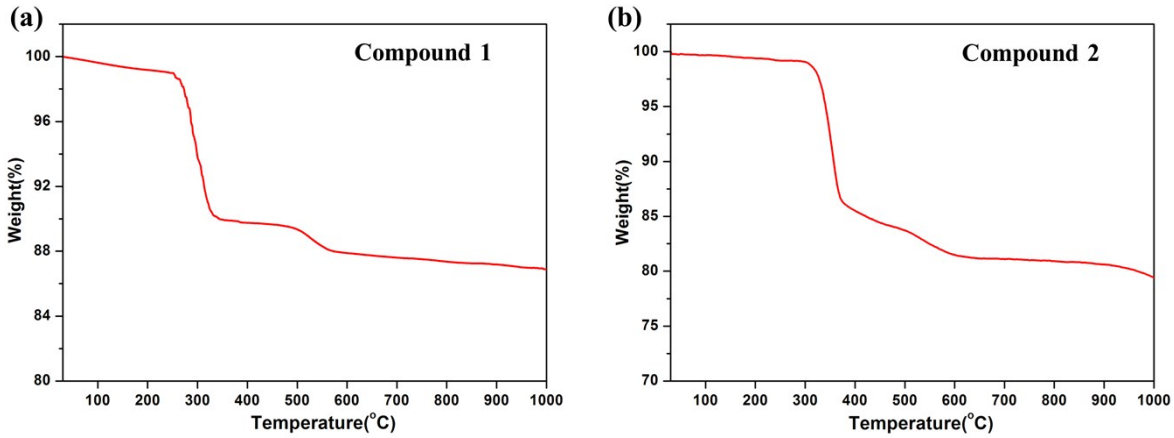

Figure S4. TG curves of compounds **1** (a) and **2** (b).

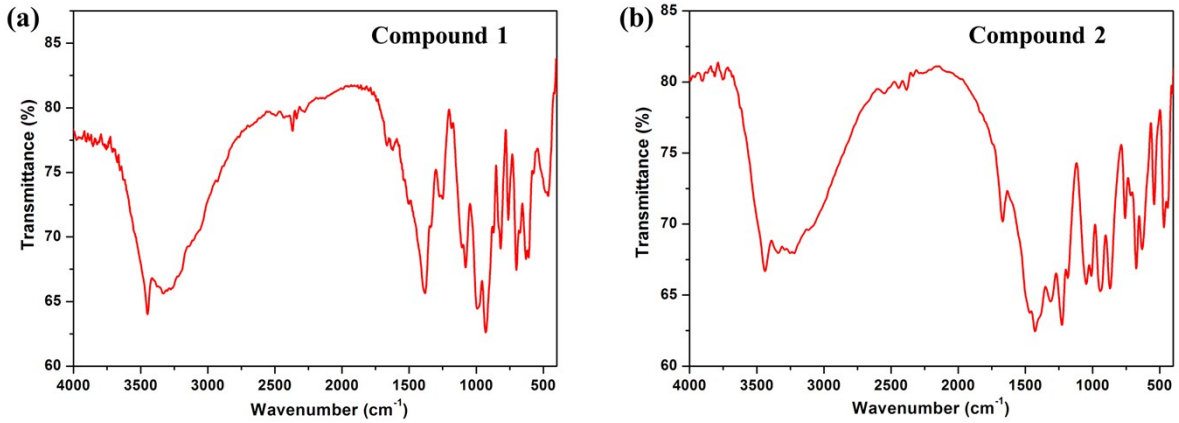

Figure S5. IR spectra of compounds **1** (a) and **2** (b).

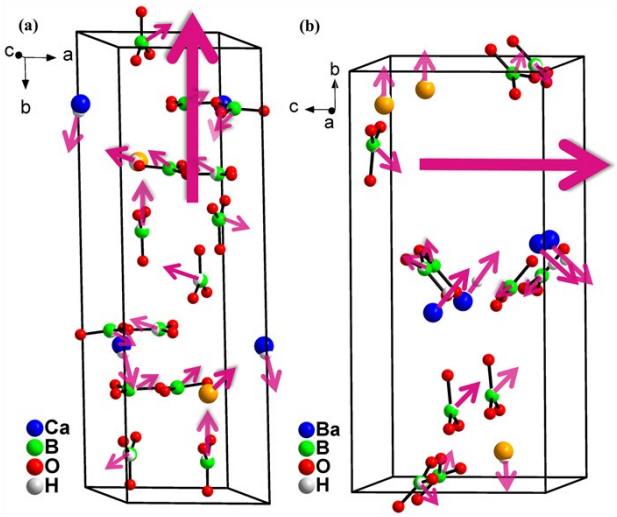

Figure S6. Ball-and-stick representation of the $CaO_{10/11}$, $BaO_{7/10}$ polyhedra (O atoms are omitted for clarity) and BO_3 units in a unit cell. Fuchsia arrows indicate the approximate directions of the distortions of $CaO_{10/11}$, $BaO_{7/10}$ polyhedra and BO_3 units. Big fuchsia arrow represent the mainly approximate direction of the net dipole moments of **1** (a) and **2** (b).