

## Supplementary material

### The effects of boron partially or fully linked with a cross-linking structure of organic precursor on purity and morphology of ZrB<sub>2</sub> powder

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The complex was dissolved in ethanol (25 mL), followed by the addition of phenolphthalein indicator. NaOH solution (0.1 mol/L) was added dropwise until the color changed (pink), and then glycerol was added before the second titration was carried out to reach a second color change (pink). The percentage content of free B-OH (D, mol%) in the complex was calculated by the volume of NaOH solution used in the second titration, and a range of analysis was conducted as shown in Table S1. In Table S1,  $K_i$  ( $i = 1, 2, 3, 4$ ) is defined as the summation of the evaluation index D from four levels for each factor. The range between the maximum and minimum K values in the column associated with the corresponding factor is specified as R. The larger the R value, the greater the relative importance of the corresponding factor.

**Table S1** Conditions and corresponding results of orthogonal experiments.

No.	Factor A Glycerol:H <sub>3</sub> BO <sub>3</sub> (mol.)	Factor B Reaction temperature (°C)	Factor C Reaction time (h)	Results (D) Free B–OH (mol%)
1	1:0.67	140	1	23.71
2	1:0.67	160	1.5	24.11
3	1:0.67	180	2	22.96
4	1:0.67	200	2.5	27.30
5	1:1	140	1.5	11.92
6	1:1	160	1	8.86
7	1:1	180	2.5	13.88
8	1:1	200	2	12.36
9	1:1.5	140	2	2.97
10	1:1.5	160	2.5	3.14

11	1:1.5	180	1	2.21
12	1:1.5	200	1.5	3.24
13	1:2	140	2.5	0.57
14	1:2	160	2	0.51
15	1:2	180	1.5	0.79
16	1:2	200	1	0.42
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K1	98.08 %	39.18 %	35.22 %	
K2	47.04 %	36.62 %	40.06 %	
K3	11.57 %	39.86 %	38.80 %	
K4	2.30 %	43.33 %	44.90 %	
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Range R	95.78 %	6.71 %	9.68 %	

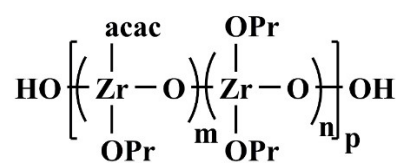


Fig. S1 Structure of PNZ.

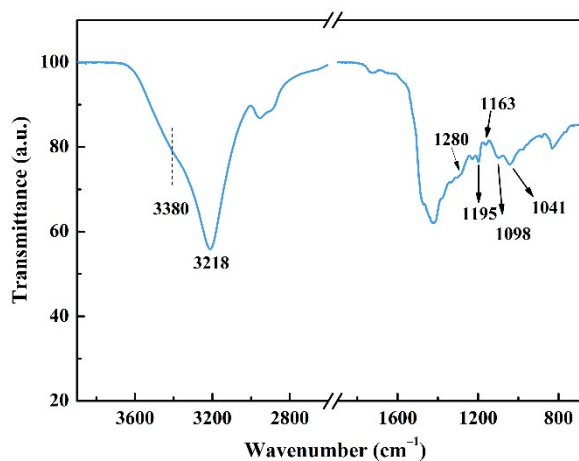
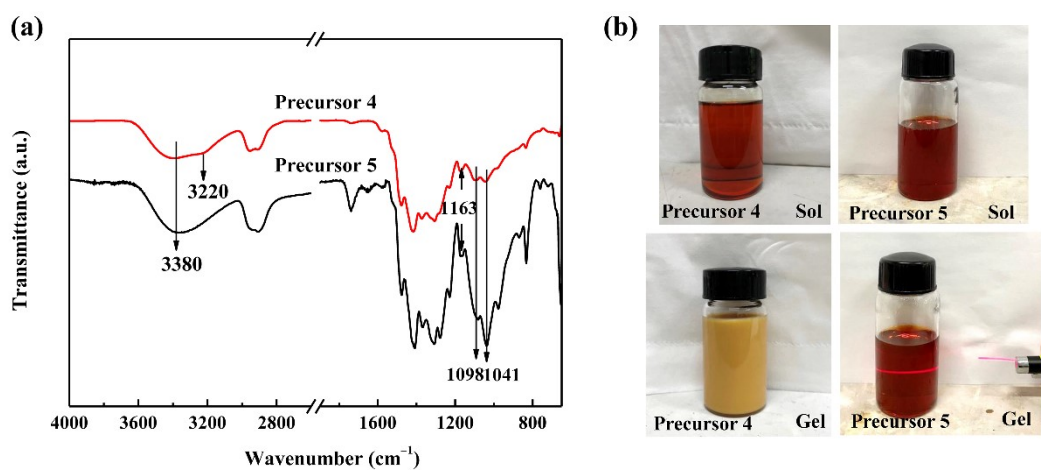


Fig. S2 FTIR spectrum of Precursor 3.



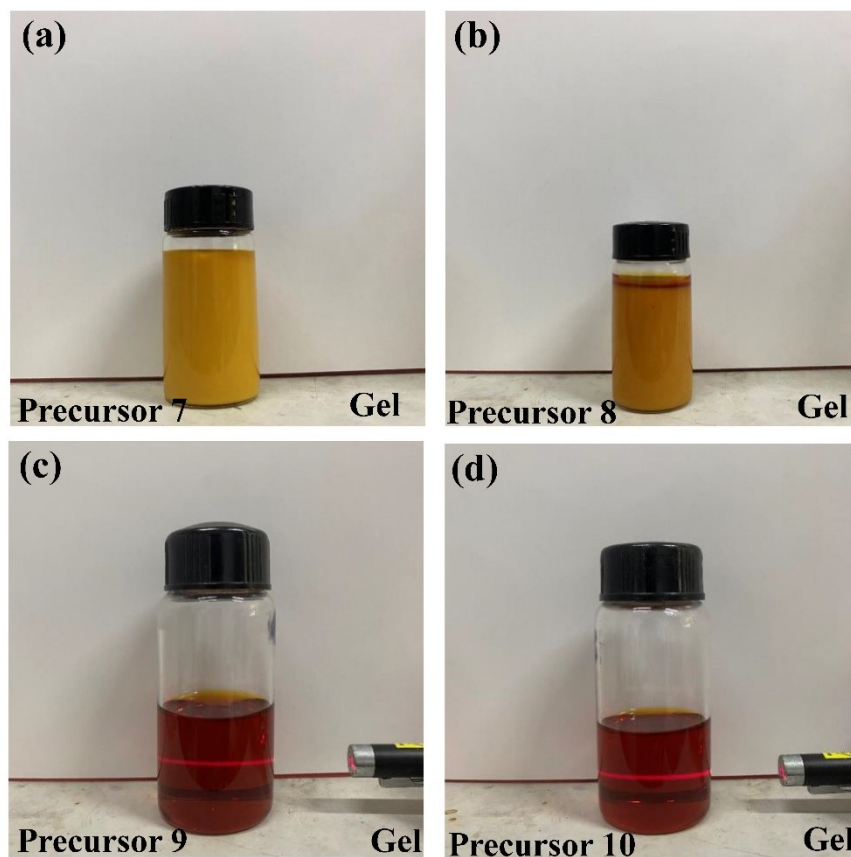
**Fig. S3** (a) FTIR spectra of Precursors 4 and 5; (b) Images of the sol and gel obtained from Precursors 4 and 5, respectively. Gel of Precursor 5 shows Tyndall effect in (b).

**Table S2** Calculated phase compositions in  $ZrB_2$  powders based on RIR method

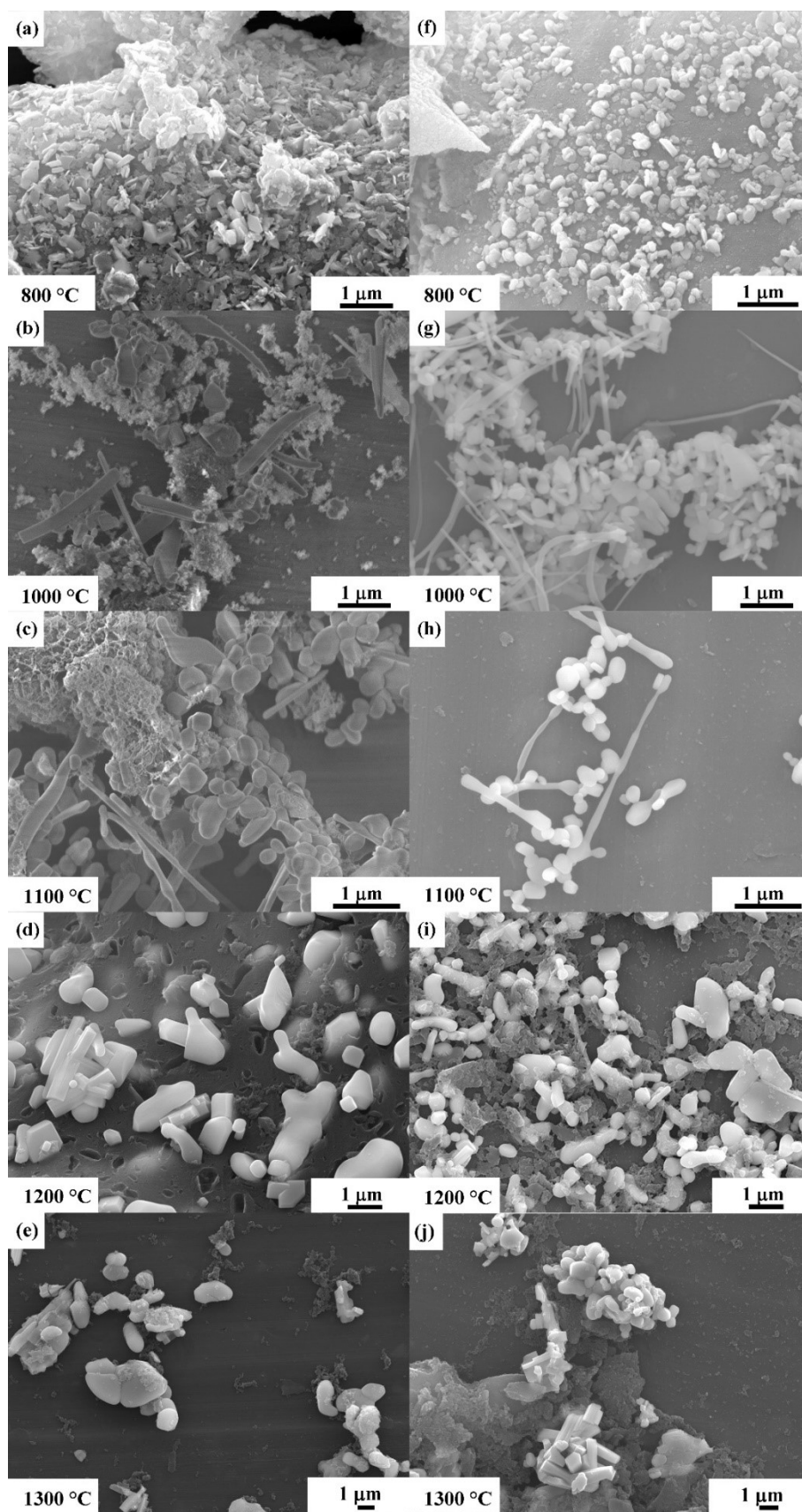
Phase weight fraction (wt.%)	Phase weight fraction		
	<i>m</i> -ZrO <sub>2</sub>	<i>t</i> -ZrO <sub>2</sub>	ZrB <sub>2</sub>
Precursor 1	6.2%	0.8%	92.9%
Precursor 2	5.8%	0.4%	93.7%



**Fig. S4** Image of the gel obtained from Precursor 6 with Tyndall effect.



**Fig. S5** Images of gels obtained from (a) Precursor 7, (b) Precursor 8, (c) Precursor 9, (d) Precursor 10. (c) and (d) shows the Tyndall effect.



**Fig. S6** SEM images of  $\text{ZrO}_2$  particles obtained from precursors after calcinated for 1 h at

different temperatures: (a-e) Precursor 4, (f-j) Precursor 5.