## Supporting Information

## Fire-Resistant, Ultralight, Superelastic and Thermal-Insulated Polybenzazole Aerogels

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Solvent A <sup>a</sup>			Dispersion B <sup>b</sup>		
MSA (g)	EA (g)	$H_2O(g)$	Concentration (wt%)	Weight (g)	
8.000	2.000	0.25	1.00		
7.900	2.100	0.26	0.75	10.0	
7.750	2.250	0.28	0.50	10.0	
7.625	2.375	0.32	0.25		

Table S1. The amounts of reagents used in the fabrication of PBO gels.

<sup>a</sup>Mixture of MSA, EA and H<sub>2</sub>O. <sup>b</sup>Dispersion of PBO nanofiber in MSA and TFA.

Table S2. The densities and corresponding porosities of PBOAs.<sup>*a*</sup>

Samples	PBOAs-1	PBOAs-2	PBOAs-3	PBOAs-4
ho (mg cm <sup>-3</sup> )	15.7±1.7	10.0±0.4	8.0±0.4	3.6±0.1
Porosity (%)	98.93±0.1 1	99.31±0.03	99.45±0.03	99.75±0.01

<sup>*a*</sup>The skeletal density of PBOAs is 1.47 g cm<sup>-3</sup>.

Samples	Density (mg cm <sup>-3</sup> )	Young's modulus (MPa)	Stress at 90% strain (MPa)
PBOAs-1	15.7	1.22±0.12	1.10±0.10
PBOAs-2	10.0	$0.40\pm0.06$	0.24±0.01
PBOAs-3	8.0	0.19±0.03	0.15±0.02
PBOAs-4	3.6	0.03±0.01	0.03±0.01

Table S3. Mechanical performance of PBOAs.



Figure S1. Statistical analysis of the diameter of PBO nanofibers according to TEM images.



Figure S2. GC-MS spectra of the mixture of MSA, TFA, EA and  $H_2O$  reacted for 24 h, followed by washing with saturated NaHCO<sub>3</sub> aqueous solutions and extraction with toluene.



Figure S3. Photographs of the PBO nanofiber sol gelated by protons consumption or in coagulation bath.



Figure S4. A controlled freezing process of PBO gels in a pre-heated oven.



Figure S5. Varied cooling rate in the freezing process.



Figure S6. SEM images of PBOAs with higher cooling rate.



Figure S7. SEM images of (a, b) PBOAs-4, (c, d) PBOAs-2 and (e, f) PBOAs-1.



Figure S8. Nitrogen adsorption-desorption isotherms of (a) PBOAs-1, (b) PBOAs-2, (c) PBOAs-3 and (d) PBOAs-4.



Figure S9. Compressive  $\sigma$ - $\epsilon$  curve of uncross-linked PBOAs. The insets are photographs showing the sample at different compressive states.



Figure S10. (a) Tensile and (b) bending stress-strain curves of PBOAs-1.



Figure S11. SEM images of PBOAs-1 (a, b) before and (c, d) after 500 loadingunloading fatigue compressive cycles at  $\varepsilon$  of 80%.



Figure S12. Compressive stress-strain curves of (a) PBOAs-4, (b) PBOAs-3, (c) PBOAs-2 and (d) PBOAs-1.



Figure S13. SEM images of PBOAs after being treated at (a, b) 300 °C and (c, d) 400 °C for 120 h.



Figure S14. SEM images of PBO/FS composite aerogels.