

## Supporting Information

# Constructing Rigid–Flexible Robust Silicone Aerogels via Hyperconnected POSS Networks for Extreme Thermal Protection

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## Part A: Detailed information of ablation test

Here, the size of ablation specimen was  $\Phi 30 \times 10$  mm. The tests were performed with 5 parallel specimens to ensure statistical significance. A K-type thermocouple was utilized to record thermal responses on the backside surfaces. The linear ablation rate ( $R_l$ ) and mass ablation rate ( $R_m$ ) were calculated by employing the following formulas:

$$R_l = (l_0 - l_t) / t \quad \backslash * \text{MERGEFORMAT (1)}$$

$$R_m = (m_0 - m_t) / t \quad \backslash * \text{MERGEFORMAT (2)}$$

Where  $l_0$  and  $m_0$  represents the thickness and mass before ablation,  $l_t$  and  $m_t$  represents the thickness and mass after ablation, and  $t$  is the ablation time.<sup>1</sup>

## Part B: Supplementary Figures and Tables

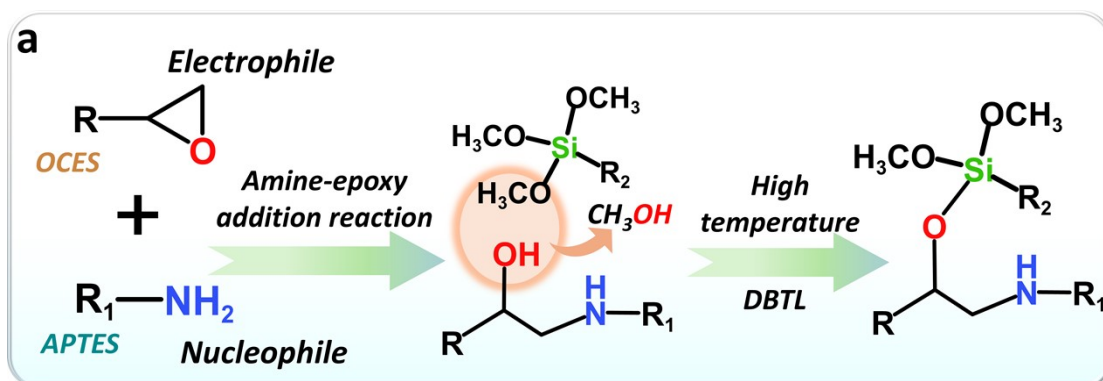


Fig. S1 Schematic of the synthesis route for POSS-SAE.

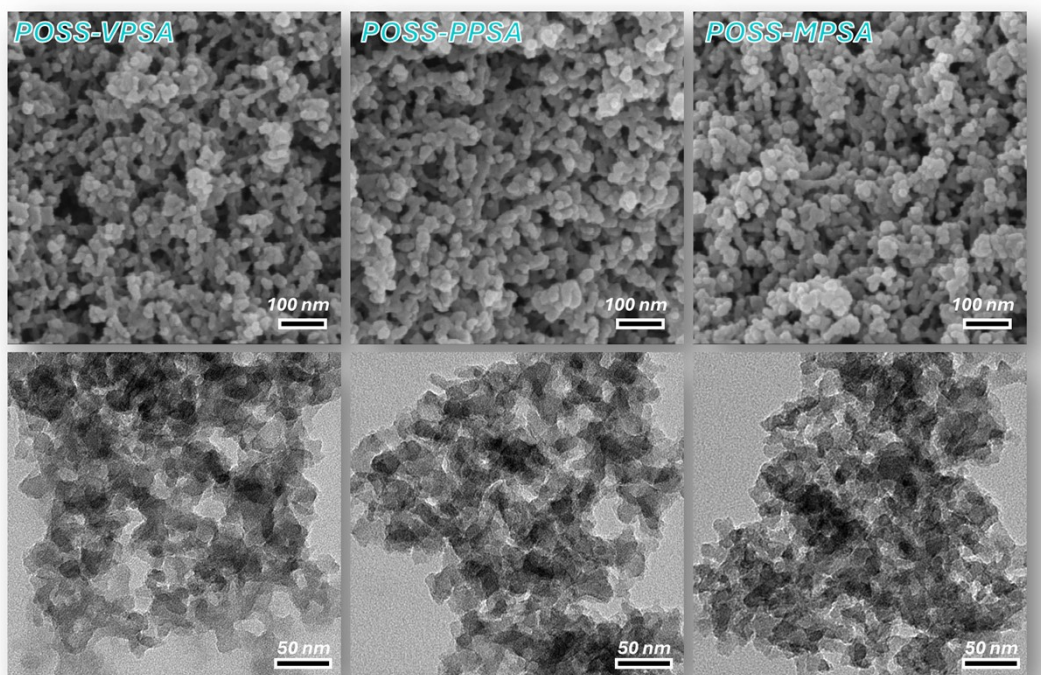


Fig. S2 SEM and TEM images of POSS-PSAs.

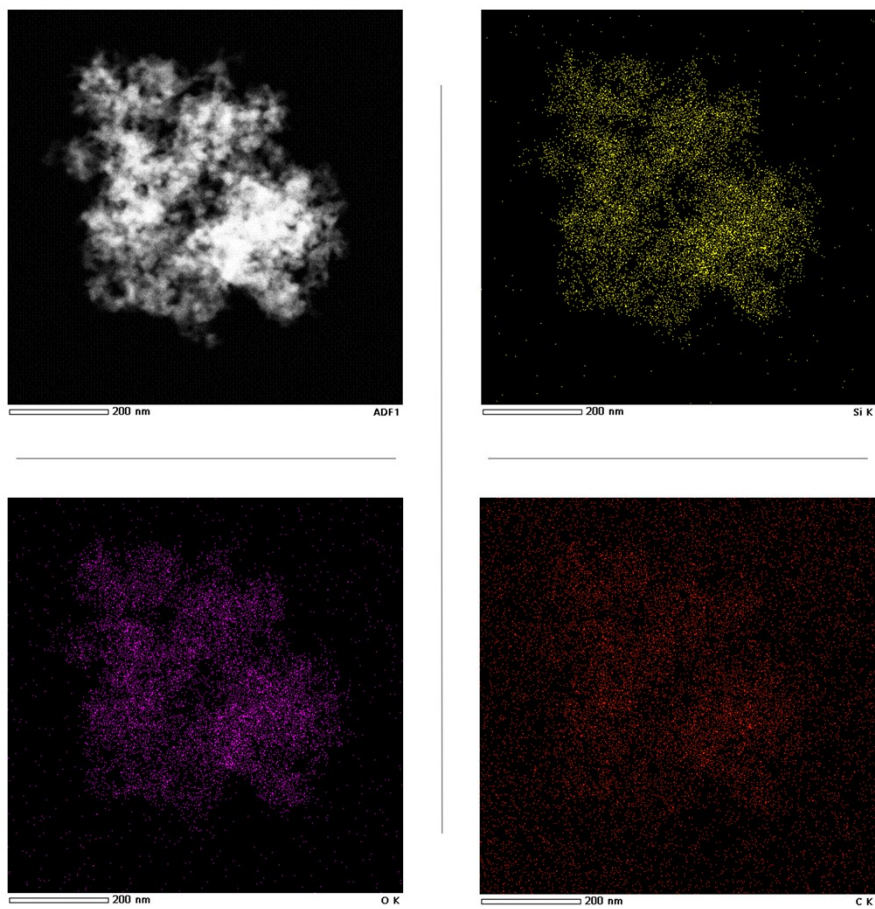


Fig. S3 Elemental mapping of POSS-VPSA.

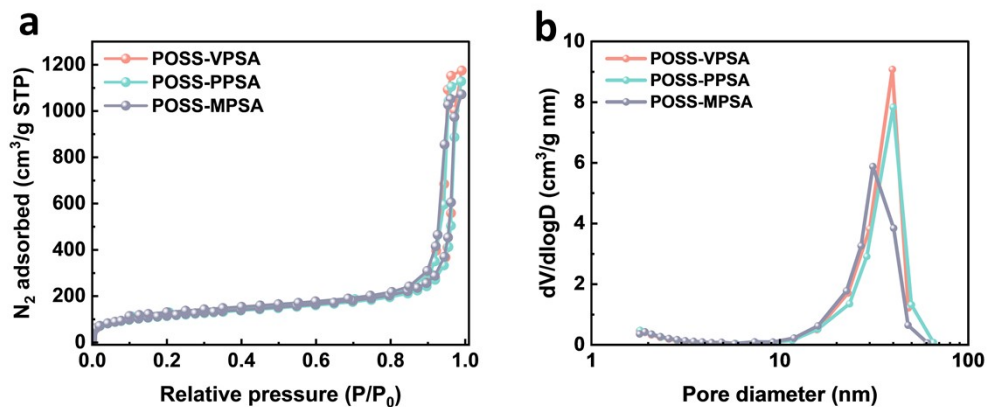


Fig. S4 BET Analysis Results of the POSS-PSAs. (a)  $N_2$  adsorption/desorption isotherms. (b) Pore size distribution.

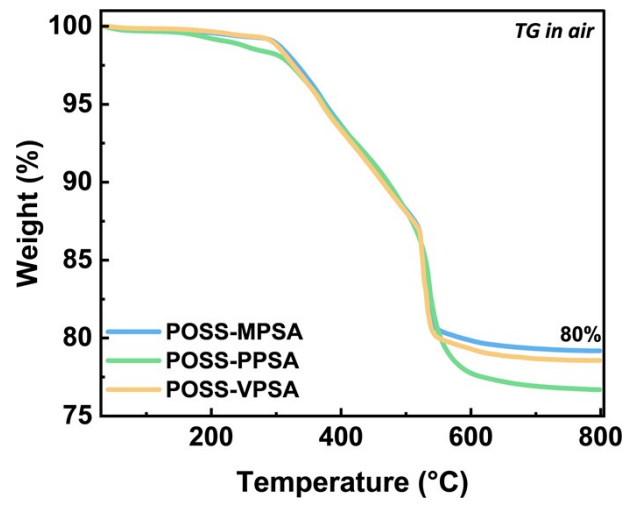


Fig. S5 TG curves of POSS-PSAs under air atmosphere.

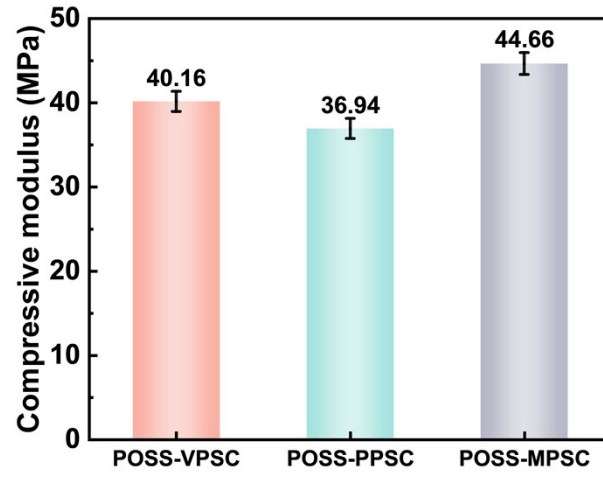


Fig. S6 Compressive modulus of POSS-PSCs.

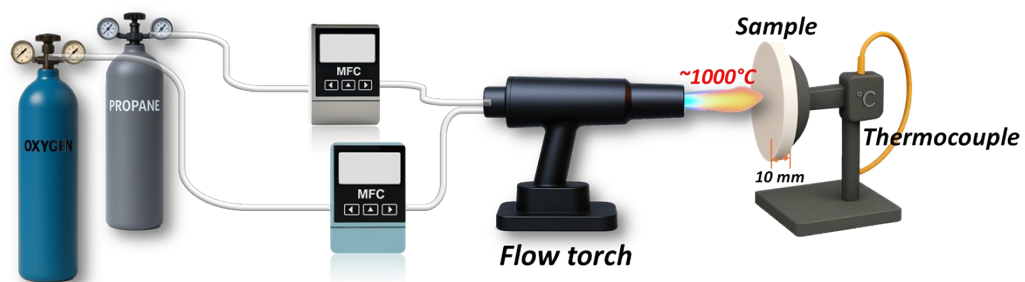


Fig. S7 Schematic diagram of oxy-propane ablation system.

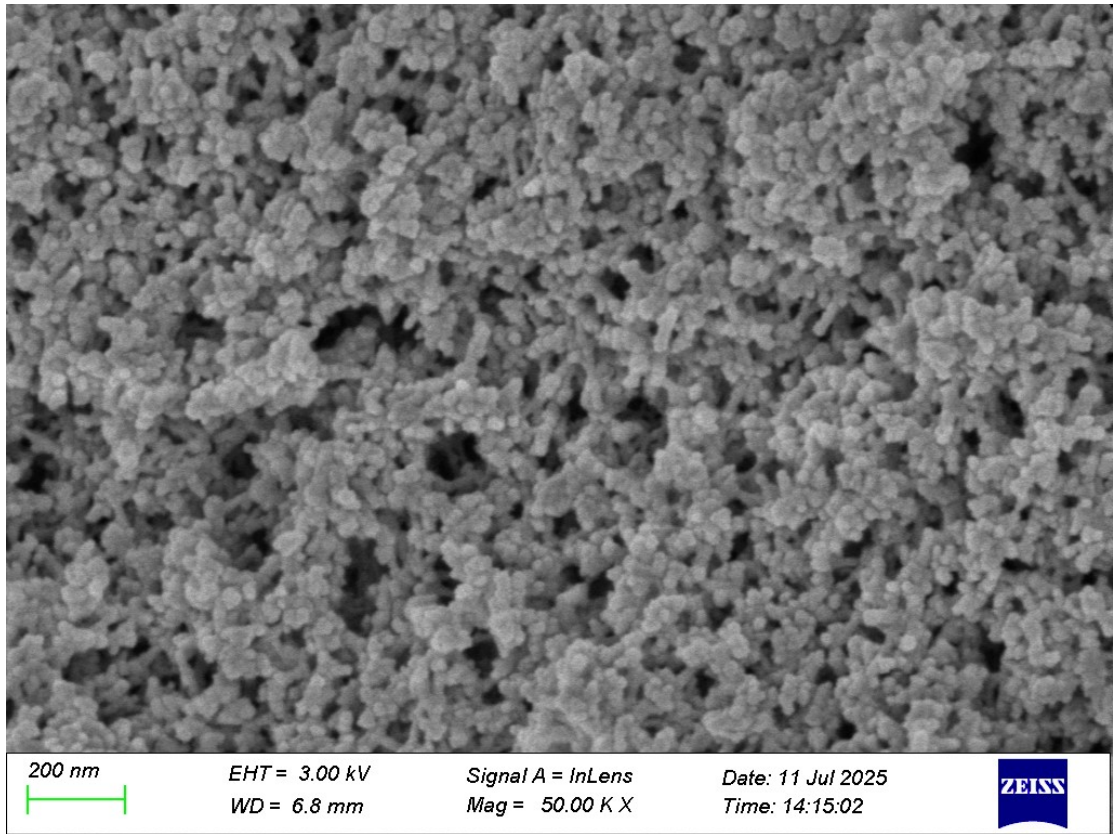


Fig. S8 SEM image of POSS-VPSC after the oxygen–propane flame ablation at 1000 °C.

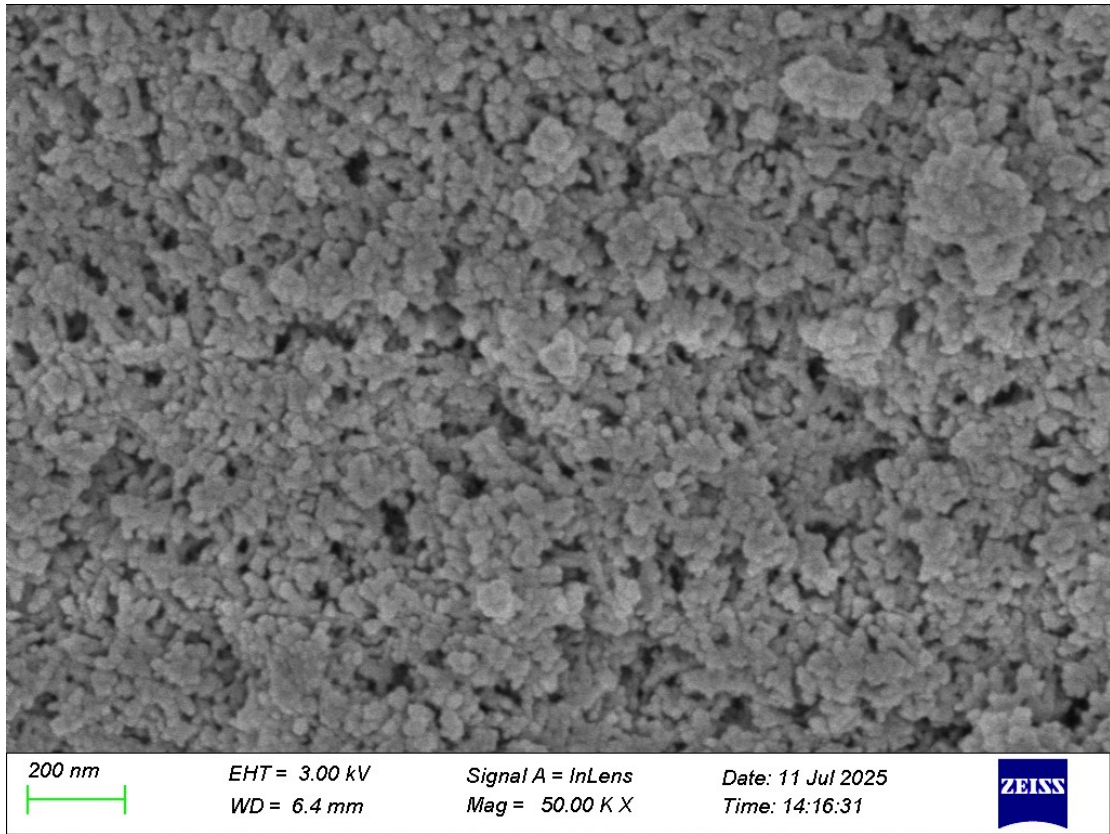


Fig. S9 SEM image of POSS-VPSC after the oxygen–propane flame ablation at 1400 °C.

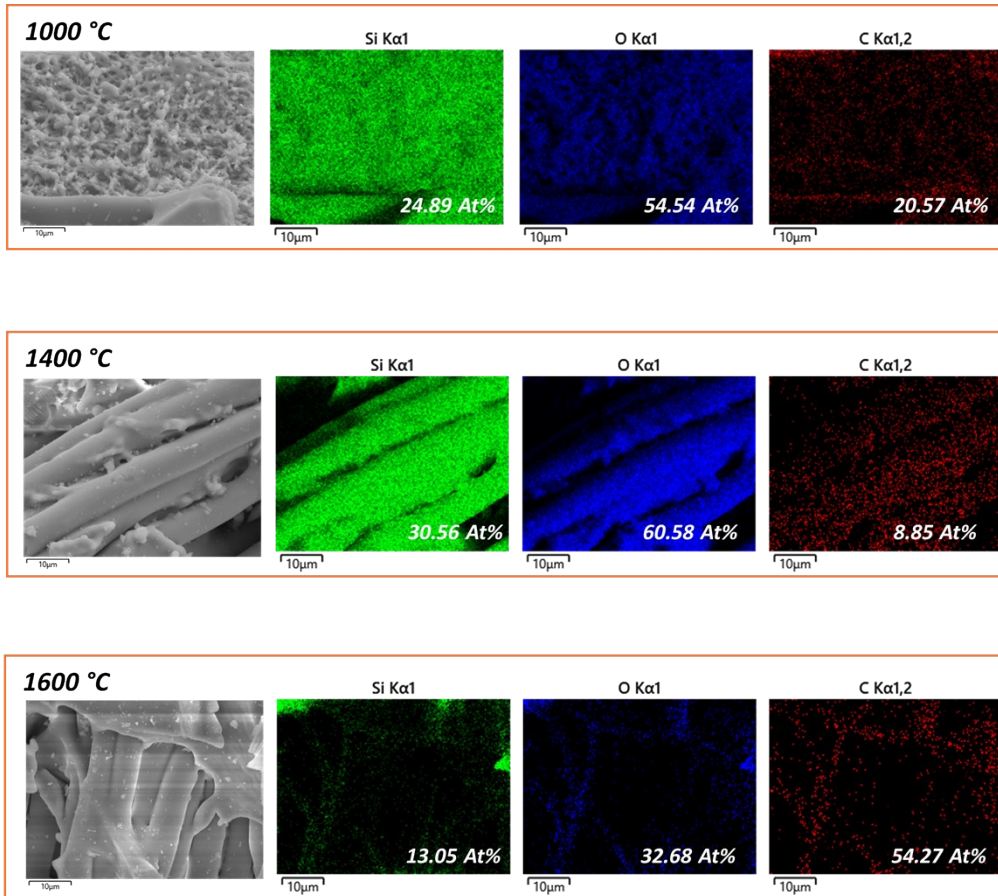


Fig. S10 SEM image and EDS elemental mappings of the POSS-VPSC composite surface after ablation at different temperatures.

**Table S1. Amount of Deionized Water for POSS-PSA Preparation with Various**

**POSS-SAEs**

POSS-SAE	Deionized Water (g)
POSS-VSAE	0.61
POSS-PSAE	0.56
POSS-MSAE	0.63

**Table S2. Typical physical properties of the aerogels**

Sample	Bulk density (g·cm <sup>-3</sup> )	Volume shrinkage (%)	Mean pore diameter <sup>a</sup> (nm)	S <sub>BET</sub> <sup>b</sup> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	λ <sup>c</sup> (W·m <sup>-1</sup> ·K <sup>-1</sup> )
POSS-VPSA	0.35	5	18.8	413	1.80	0.036
POSS-PPSA	0.34	4	19.5	412	1.72	0.035
POSS-MPSA	0.37	8	17.6	421	1.64	0.038

<sup>a</sup>Mean pore diameter obtained from nitrogen adsorption branch via the Barrett–Joyner–Halenda method. <sup>b</sup>Brunauer–Emmett–Teller SSA obtained from nitrogen adsorption measurement. <sup>c</sup>Thermal conductivity at room temperature and ambient pressure.

**Table S3. Typical physical properties of the composites**

Sample	Bulk density (g/cm <sup>3</sup> )	Volume shrinkage (%)	Compressive modulus (MPa)	$\lambda^c$ (W·m <sup>-1</sup> ·K <sup>-1</sup> )
POSS-VPSC	0.50	3	55.5	0.037
POSS-PPSC	0.49	2	52.8	0.036
POSS-MPSC	0.52	5	58.4	0.038

**Table S4 Detailed comparison of mechanical and thermal properties of various aerogels (corresponding to Fig. 4g)**

Sample	Bulk density (g/cm <sup>3</sup> )	Compressive Strength (MPa)	Thermal Conductivity (W·m <sup>-1</sup> ·K <sup>-1</sup> )	Test Conditions	Ref.
POSS-MPSA	0.37	6.10	0.038	RT <sup>a</sup>	This Work
MK/SiO <sub>2</sub> aerogel	0.29	3.24	0.031	RT <sup>a</sup>	2
PMMS/PMDMS silicone aerogel	0.42	5.83	0.052	RT <sup>a</sup>	3
SiO <sub>2</sub> NWs-reinforced silica aerogel	~0.12	~1.38 <sup>b</sup>	0.037	RT <sup>a</sup>	4
Chitosan/silica hybrid aerogel	0.17	~0.24 <sup>c</sup>	0.028	RT <sup>a</sup>	5

<sup>a</sup> Room temperature; <sup>b</sup> Compressive stress recorded at 60% strain; <sup>c</sup> Compressive stress recorded at 5% strain

**Table S5 Detailed comparison of mechanical and thermal properties of various composites (corresponding to Fig. 5e)**

Sample	Fiber Content (wt%)	Bulk density (g/cm <sup>3</sup> )	Tensile Strength (MPa)	Thermal Conductivity (W·m <sup>-1</sup> ·K <sup>-1</sup> )	Test Conditions	Ref.
POSS-MPSC	38.5	0.52	27.8	0.038	RT <sup>a</sup>	This Work
Silicone/ Quartz fiber composites	40.0	0.50	15.5	0.039	RT <sup>a</sup>	6
Silicone/fibrous ceramic tile	66.7	0.45	3.6	0.06	RT <sup>a</sup>	7
Fiber-reinforced alumina–silica aerogel composites	38.5	0.39	1.8	0.039	RT <sup>a</sup>	8
Silicone/phenolic/ quartz/carbon hybrid fiber	57.6	0.33	16.8	0.062	RT <sup>a</sup>	9
SiO <sub>2</sub> /quartz fiber	48.3	0.58	4.3	0.042	RT <sup>a</sup>	10

<sup>a</sup> Room temperature

## Reference

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