

Supplementary Information

High ionic conduction in a robust anionic metal–organic framework containing Mg^{2+} under guest vapors

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Synthesis of SU-102 ($\{(\text{CH}_3)_2\text{NH}_2\}_2[\text{Zr}(\text{C}_{14}\text{H}_3\text{O}_8)_2]$)

A mixture of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (1600 mg, 5 mmol), ellagic acid dihydrate (3382 mg, 10 mmol), 100 mL DMF, 50 mL H_2O , and 75 mL acetic acid was refluxed at 80 °C for 48 h. The precipitate was collected by centrifugation and washed with 30 mL DMF (16 times repetition of the washing and centrifugation) and 30 mL MeOH (7 times repetition of the washing and centrifugation). The obtained powder was dried under vacuum at 130 °C overnight (green powder, 2.97 g, 3.80 mmol, yield: 76%).

(Ref. 1) E. S. Grape, A. K. Inge, et al., *Nat. Water*, 2023, **1**, 433–442.

Synthesis of $\text{Mg}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$ (TFSI⁻ = Bis(trifluoromethanesulfonyl)imide)

Mg powder (1.1 g, 45 mmol) was added in an aqueous solution (H_2O 100 mL) of HTFSI (22.4 g, 80 mmol) and the mixture was stirred at room temperature for 90 min. The remaining Mg powder was removed by filtration. The solvent in the filtrate was removed by evaporation. The obtained white powder was dried under vacuum at 160 °C for 8 hours (white powder, 24.8 g, 34 mmol, yield: 85%).

Synthesis of SU-102-Mg ($\text{Mg}[\text{Zr}(\text{C}_{14}\text{H}_3\text{O}_8)_2]$)

SU-102 (1.00 g, 1.28 mmol) was immersed in 1 M acetonitrile solution of Mg(TFSI)₂ (20 mL) for 4 days at room temperature (the solution was exchanged to a fresh solution every day). After collecting the powder by centrifugation, it was immersed in acetonitrile solvent (30 mL) for a day at room temperature (the solvent was exchanged to a fresh solvent three times). The target compound was collected by centrifugation and dried at 100 °C under vacuum overnight (green powder, 1.06 g, 1.00 mmol, yield: 78%). Elemental analysis for Mg[Zr(C₁₄H₃O₈)₂](H₂O)₁₆; Calcd C 33.56%, H 3.82%, Mg 2.43% (by ICP-AES); Found C 33.69%, H 3.56%, Mg 2.64% (by ICP-AES).

Physical measurements

X-ray powder diffraction (XPRD) patterns were collected using MiniFlex600 ($\lambda = 1.54059$; Cu- $K\alpha$) (Rigaku, Inc.) at room temperature. Solution-phase ¹H-NMR spectra were measured with AVANCE NEO 400 (Bruker, Inc.) spectrometer at room temperature. The MOF samples were digested in DCI/D₂O/DMSO-d₆. Adsorption isotherms for N₂ (at 77 K) and MeCN (at 298 K) were measured using TriStar II 3020 (Micromeritics, Inc.) and BELSORP-max (Microtrac BEL, Inc.). The samples were preliminarily dehydrated at 130 °C under vacuum overnight. Thermogravimetric analysis (TGA) curves were measured using TG-DTA8122/S (Rigaku, Inc.) with a heating rate of 5 °C min⁻¹. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) experiments were performed with SPS3520UV (SII nanotechnology, Inc.). Ionic conductivity was estimated by alternating current impedance spectroscopy with Solartron 1260/1296A impedance analyzer with the frequency range 1–10M Hz. The samples were sandwiched by porous Au as the blocking electrodes in a home-made sealed cell connecting to gas lines. The temperature of the sample was controlled by an incubator, SU-222 (Espec, Inc.). Before the impedance measurements under the vapor of various anhydrous organic solvents, the sample was dehydrated at 130 °C under dry N₂ gas flow overnight. The resistance of the sample was estimated by a semicircle fitting of the obtained Nyquist plots. *In situ* Fourier transform infrared (FT-IR) spectra were measured using JASCO FT/IR-4200 with a mercury–cadmium–telluride detector at 30 °C. A self-supporting disc (2 cm ϕ) was prepared by pressing the MOF sample (~40 mg). The disc was put in the quartz IR cell with CaF₂ windows connected to a gas line. The sample disc was dehydrated at 130 °C under He flow (100 cm³ min⁻¹) overnight before the measurements. After cooling to 30 °C under He flow, 2 μ L of MeCN was injected to the sample. Spectra were measured accumulating 20 scans at a resolution of 4 cm⁻¹. A reference spectrum taken at 30 °C under He flow was subtracted from each spectrum.

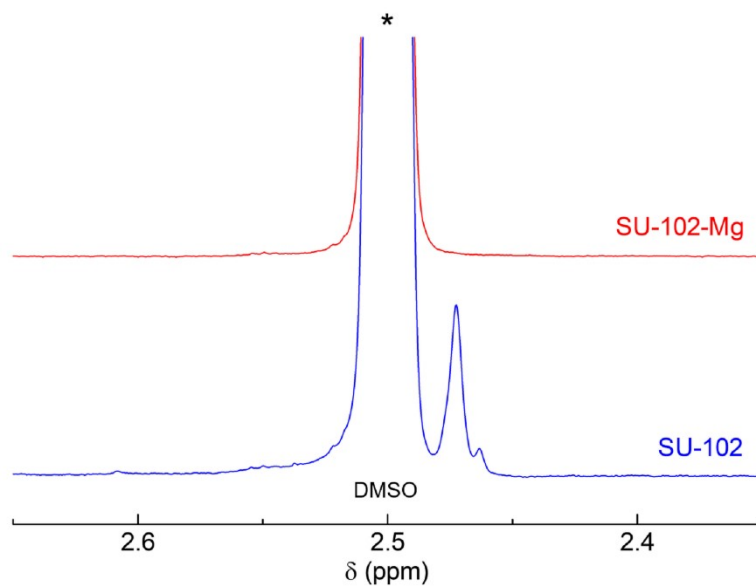


Figure S1. Solution phase ¹H-NMR spectra of SU-102 and SU-102-Mg. The samples were digested in DCI/D₂O/DMSO-d₆.

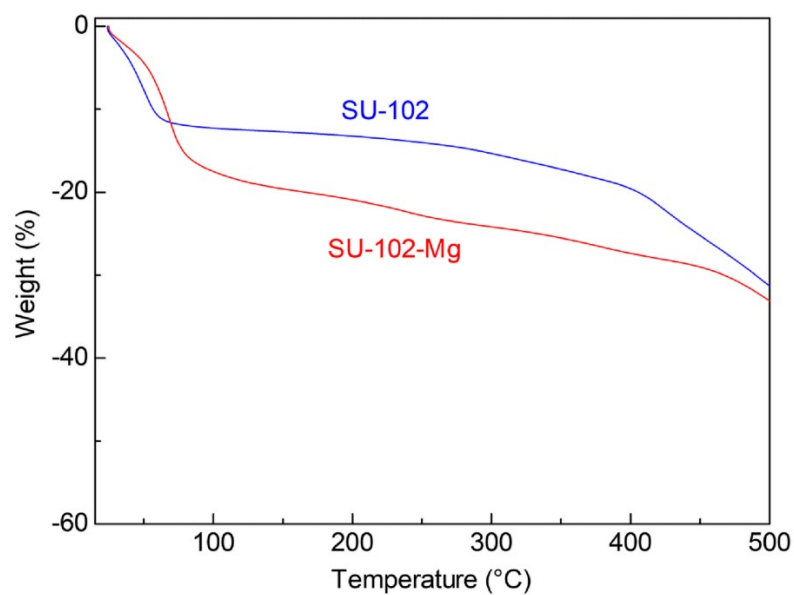


Figure S2. TGA curves of SU-102 and SU-102-Mg.

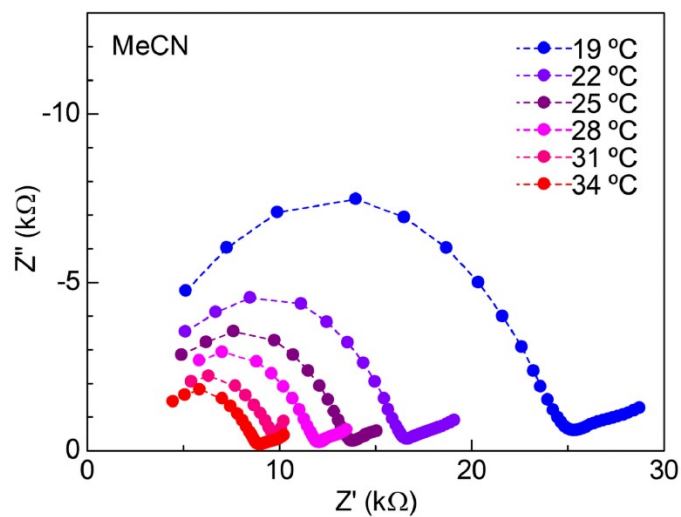


Figure S3. Nyquist plots of SU-102-Mg under the guest vapor (exemplified by MeCN, $P/P_0 = 1$).

Table S1. Activation energy of SU-102-Mg under various guest vapors.

Guest molecule	MeOH	MeCN	EtOH	THF	N ₂
Activation energy (eV)	0.31	0.54	0.39	0.71	0.72

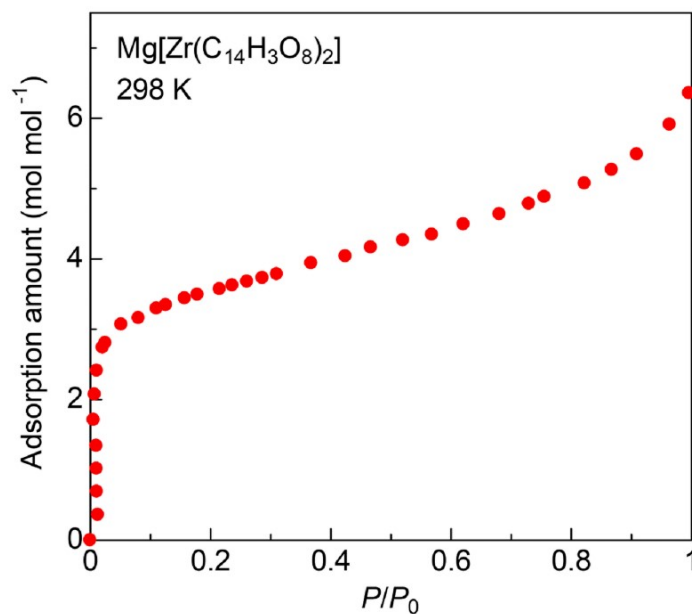


Figure S4. Adsorption isotherms of SU-102-Mg for MeCN vapor at 298 K.

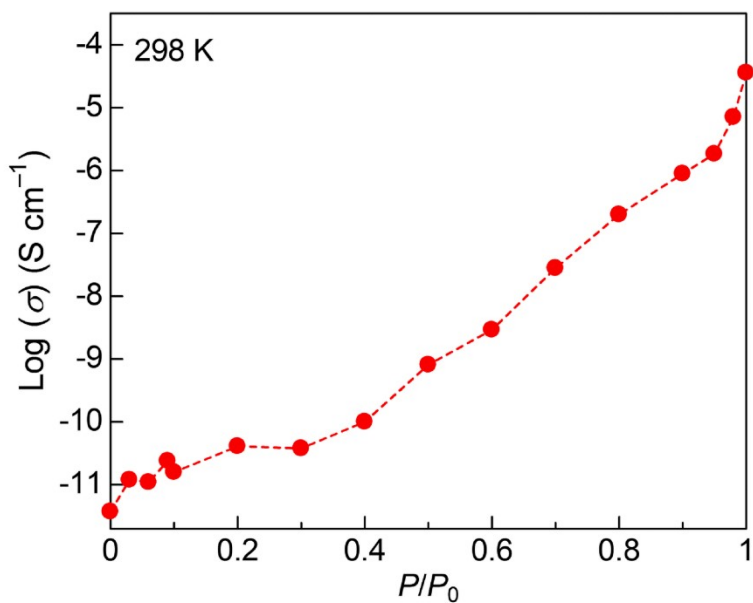


Figure S5. Dependence of ionic conductivity on partial pressure of MeCN vapor (SU-102-Mg, 298 K).

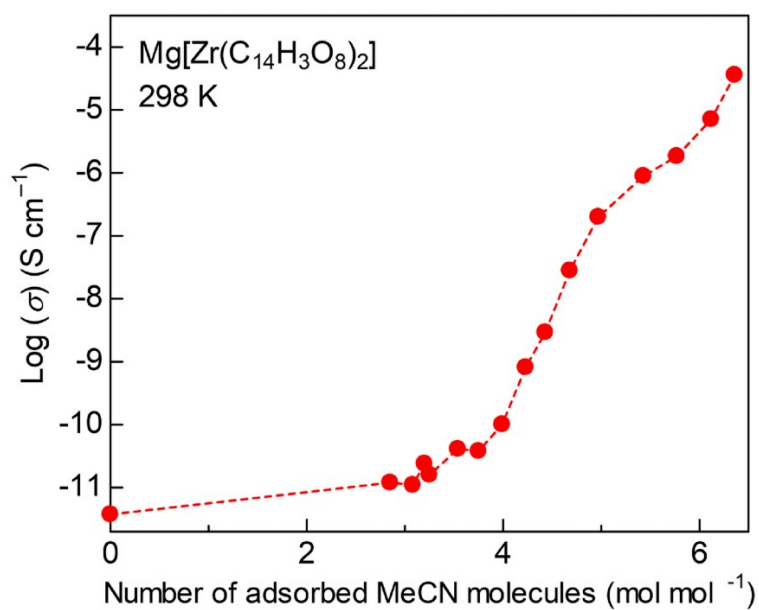


Figure S6. Relationship between the ionic conductivity and the number of adsorbed MeCN molecules (SU-102-Mg, 298 K).

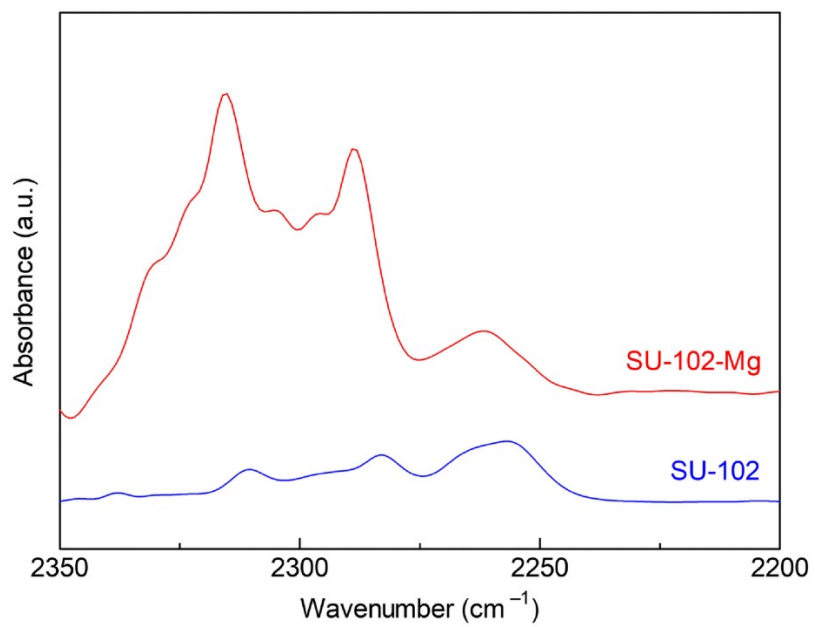


Figure S7. *In situ* IR spectra of SU-102 and SU-102-Mg under MeCN vapor.