

Supplementary Information

Preparation of a Mg²⁺-Included MOF through Ion Exchange and its High Ionic Conductivity

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Synthesis of {N(C₄H₉)₄}₄(α-Mo₈O₂₆)

[N(C₄H₉)₄]₄(α-Mo₈O₂₆) was prepared as a precursor for MOF-688 synthesis, according to the literature.¹ Molybdenum (VI) oxide (3.612 g 24.9 mmol) was added to 30 mL of aqueous solution of tetrabutylammonium hydroxide (10%) and the mixture was stirred at room temperature for 4 days. The white precipitate was collected by filtration. It was dried under vacuum at room temperature in the presence of P₂O₅ near the sample. The obtained powder (approx. 5.61 g) was dissolved in 45 mL of acetonitrile and the insoluble precipitate was removed by filtration. After that, the filtrated solution was kept at -25 °C in a freezer for 5 days. The white precipitate was collected by filtration and dried under vacuum at room temperature in the presence of P₂O₅ near the sample (2.774 g, 1.29 mmol, yield 41%). IR (400 – 1000 cm⁻¹): 501 (m), 562 (m), 659(vs), 792 (s), 851 (m), 902 (vs), 918 (vs), 950 (m).

(Ref. 1) S. Ikegami, A. Yagasaki, *Materials*, 2009, **2**, 869–875.

Synthesis of {N(C₄H₉)₄}₃[MnMo₆O₁₈{(OCH₂)₃CNH₂}₂] (NBu₄-Mn-Mo₆)

Mn-Mo₆ was synthesized as the precursor of MOF-688 according to the literature.² The mixture of {N(C₄H₉)₄}₄(α-Mo₈O₂₆) (2.668 g, 1.2 mmol), manganese (III) acetate dihydrate (0.493 g, 1.9 mmol), tris(hydroxymethyl)aminomethane (0.523 g, 4.2 mmol), and acetonitrile (50 mL) was refluxed for 16

hours. After cooling to room temperature, the precipitate was removed by filtration. The filtrate was exposed to diethyl ether vapor in a sealed vial at room temperature. After 2 hours, the obtained white precipitate was removed by filtration. After that, the filtrate solution was again exposed to the diethyl ether vapor in a sealed vial and kept at room temperature for 4 days. The orange powder was collected by filtration (0.812 g, 0.43 mmol, yield 26%).

(Ref. 2) P. R. Marcoux, B. Hasenknopf, J. Vaissermann, P. Gouzerh, *Eur. J. Inorg. Chem.*, 2003, **13**, 2406–2412.

Synthesis of tetrakis(4-formylphenyl)methane (TFPM)

TFPM was synthesized as the precursor of MOF-688 according to the literature.³ THF (500 mL) solution of tetrakis(4-bromophenyl)methane (TBPM) (1.12 g, 1.76 mmol) was cooled down to $-78\text{ }^{\circ}\text{C}$. After that, *n*-hexane solution of *n*-butyllithium (1.6 M) (10 mL, 16 mmol) was slowly added to the cooled solution with stirring. After stirring it at $-78\text{ }^{\circ}\text{C}$ for 30 min, anhydrous N,N-dimethylformamide (DMF) (2.5 mL, 32 mmol) was added and the resulting mixture was stirred at room temperature for a night. After that, 20 mL of 1 M HCl was added to the reaction solution. The solution was evaporated to remove the THF solvent (white powder was observed.). The mixture was extracted by ethyl acetate and the organic layer gave white powder through evaporation. The white powder was dissolved in ethyl acetate and the target compound was obtained by the recrystallization (0.405 g, 0.94 mmol, yield 52%).

(Ref. 3) Z. Li, H. Li, X. Guan, J. Tang, Y. Yusran, Z. Li, M. Xue, Q. Fang, Y. Yan, V. Valchev, S. Qiu, *J. Am. Chem. Soc.*, 2017, **139**, 17771–17774.

Synthesis of MOF-688

MOF-688 was synthesized according to the literature.⁴ TFPM (40 mg, 0.09 mmol), Mn–Mo₆ (350 mg, 0.18 mmol), anhydrous 1,4-dioxane (3.5 mL), anhydrous acetonitrile (3.5 mL), and acetic acid (0.2 mL) was introduced in a pyrex tube (o.d. 13 mm ϕ , i.d. 10 mm ϕ). The reaction mixture was frozen at 77 K in a liquid N₂ bath and then the glass tube was sealed off under vacuum, resulting in a sealed glass tube (with the length of approx. 27 cm) including the reaction mixture. The reaction mixture was heated at 100 $^{\circ}\text{C}$ for 2 days. The obtained precipitate was collected by filtration. The precipitate was immersed in DMF (25 mL) at room temperature for 2 days (The solvent was exchanged four times.) and in anhydrous acetonitrile (25 mL) at room temperature for 3 days. (The solvent was exchanged six times.). The powder sample was collected and dried at room temperature under vacuum (322 mg, 0.074 mmol, yield 82%). Elemental

analysis for $\{N(C_4H_9)_4\}_6[(MnMo_6O_{18})_2C\{C_6H_4CH=NC(CH_2O)_3\}_4](CH_3CN)_3(H_2O)_3$: Calcd. C 41.04%, H 6.44%, N 4.23%; Found C 40.79%, H 6.27%, N 4.18%.

(Ref. 4) W. Xu, X. Pei, C. S. Diercks, H. Lyu, Z. Ji, O. M. Yaghi, *J. Am. Chem. Soc.*, 2019, **141**, 17522–17526.

Synthesis of $Mg(TFSI)_2 \cdot 8H_2O$ ($TFSI^- = (CF_3SO_2)_2N^-$)

$Mg(TFSI)_2 \cdot 8H_2O$ was synthesized according to the literature.⁵ A mixture of magnesium powder (1.458 g, 60 mmol), bis(trifluoromethanesulfonyl)imide (HTFSI) (28.12 g, 100 mmol), and water (125 mL) was stirred at room temperature for 90 min. Remaining magnesium powder was removed by filtration. The white powder was obtained by evaporating the filtrate solution and it was dried at 160 °C under vacuum for 8 hours (26.71 g, 37 mmol, yield 73%).

(Ref. 5) M. J. Earle, U. Hakala, B. J. McAuley, M. Nieuwenhuyzen, A. Ramani, K. R. Seddon, *Chem. Commun.*, 2004, 1368–1369.

Synthesis of MOF-688-Mg

MOF-688-Mg was synthesized through an ion exchange reaction with MOF-688. The powder sample of MOF-688 (303 mg, 0.069 mmol) was immersed in 6 mL of 1 M acetonitrile solution of $Mg(TFSI)_2$ at room temperature for 5 days. During the reaction, the solution was repeatedly exchanged to the fresh solution (totally four times). After that, the sample was immersed in fresh anhydrous acetonitrile (15 mL) at room temperature for 2 days to remove the remaining $Mg(TFSI)_2$ located inside or outside the MOF. The solution was repeatedly exchanged during the washing (totally five times). The resulting powder was collected by filtration and dried at room temperature under vacuum (205 mg, 0.061 mmol, yield 88%). Elemental analysis for $Mg_3[(MnMo_6O_{18})_2C\{C_6H_4CH=NC(CH_2O)_3\}_4](H_2O)_{30}$: Calcd. C 16.46%, H 3.19%, N 1.71%; Found C 16.13%, H 3.20%, N 1.65%.

Synthesis of MOF-688-Mg-NBu₄ (Re-introduction of NBu⁴⁺)

The powder of MOF-688-Mg (33 mg, 0.01 mmol) was immersed in 15 mL of acetonitrile solution of tetrabutylammonium chloride (1 M) and kept it at 130 °C for 2 days. After that, the sample was collected by filtration and washed by anhydrous acetonitrile, followed by air drying.

Physical measurements

X-ray powder diffraction (XPRD) measurements were performed using MiniFlex600 ($\lambda = 1.54059$; Cu- $K\alpha$) (Rigaku, Inc.) at room temperature. Solution-phase $^1\text{H-NMR}$ spectra were recorded using JNM-ECA500II (JEOL, Inc.) spectrometer at room temperature. Fourier transform infrared spectroscopy (FT-IR) was performed through an attenuated total reflection (ATR) method using FT/IR4600 spectrometer (JASCO, Inc.) at room temperature. Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) experiments were carried out on Spectro Arcos (Hitachi High-Tech Science, Inc.). Adsorption isotherms were measured using BELSORP-max (Microtrac BEL, Inc.) and TriStar II 3020 (Micromeritics, Inc.) after the sample was dried at $130\text{ }^\circ\text{C}$ under vacuum for a night.

Conductivity measurements

Ionic conductivity was estimated from alternating current (ac) impedance spectra of the sample. The ac impedance spectra were measured using Solartron 1260/1296A impedance analyzer with a home-made sealed cell, which is connected to a gas line with a mass flow controller.⁶ The pelleted sample was sandwiched with porous silver electrodes as the blocking electrodes. The sample resistance (R) was estimated by a simple semicircle fitting of the Nyquist plots. Ionic conductivity (σ) was calculated by following equation:

$$\sigma = \frac{L}{RS}$$

where L and S correspond to length of the sample pellet and cross-section area of the sample pellet, respectively. The activation energy, E_a , was estimated by Arrhenius plots of the ionic conductivity using following equation:

$$\sigma T = A \exp\left(-\frac{E_a}{kT}\right)$$

where A , k , and T correspond to pre-exponential factor, Boltzmann constant, and absolute temperature, respectively. The sample was completely dehydrated under dry N_2 gas at $130\text{ }^\circ\text{C}$ for a night before all of measurements. After cooling down to room temperature, vapor of anhydrous organic solvent was introduced into the measurement cell. The temperature was controlled by an incubator, SU-222 (Espec, Inc.).

(Ref. 6) Y. Yoshida, K. Kato, M. Sadakiyo, *J. Phys. Chem. C*, 2021, **125**, 21124–21130.

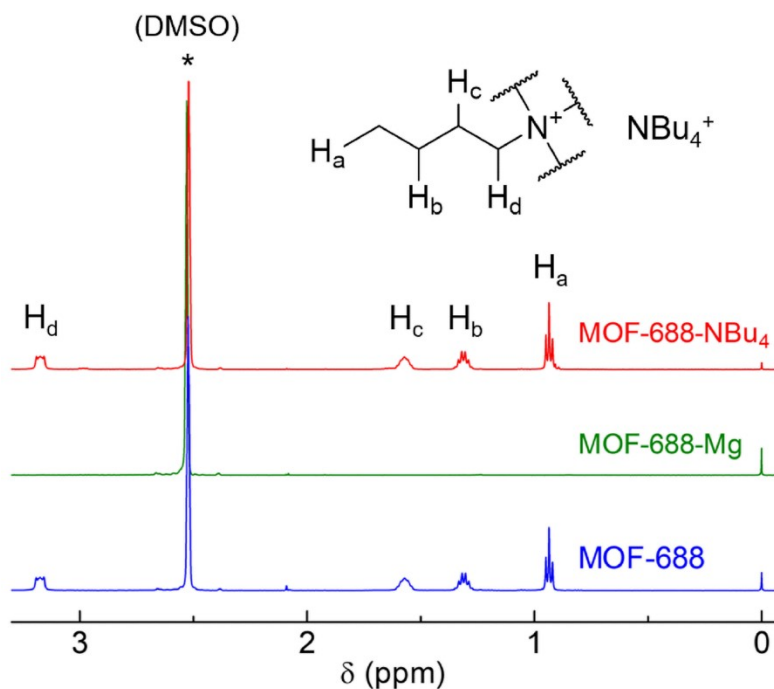


Figure S1. Solution-phase $^1\text{H-NMR}$ spectra of (blue) MOF-688, (green) MOF-688-Mg, and (red) MOF-688-NBu₄. The samples were dissolved in a mixed solvent of DMSO-d₆/DCI/D₂O.

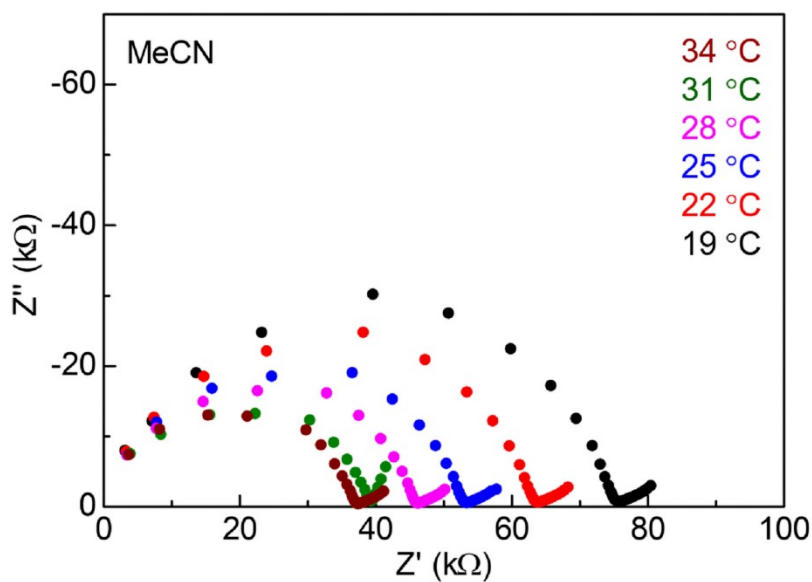


Figure S2. Nyquist plots of MOF-688-Mg at 19–34 °C, exemplified by the sample under MeCN vapor.

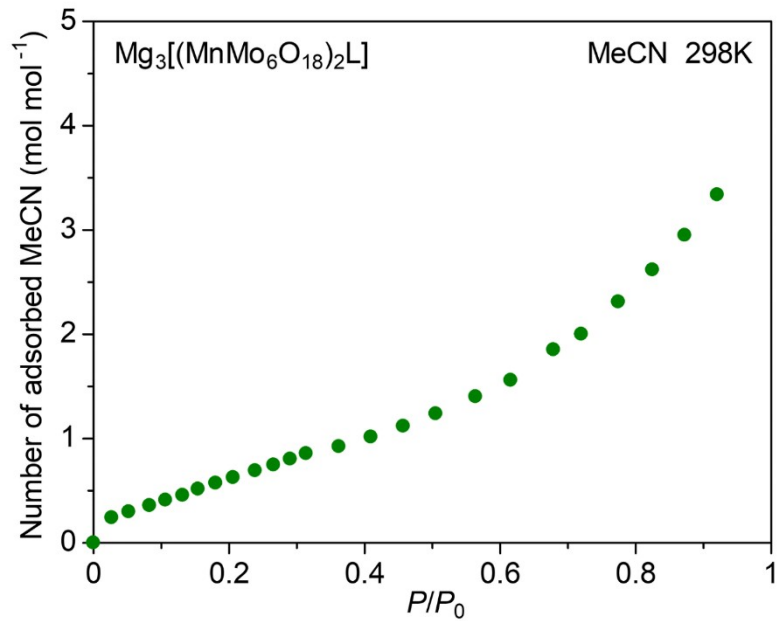


Figure S3. Adsorption isotherms of MOF-688-Mg for MeCN vapor at 25 °C.

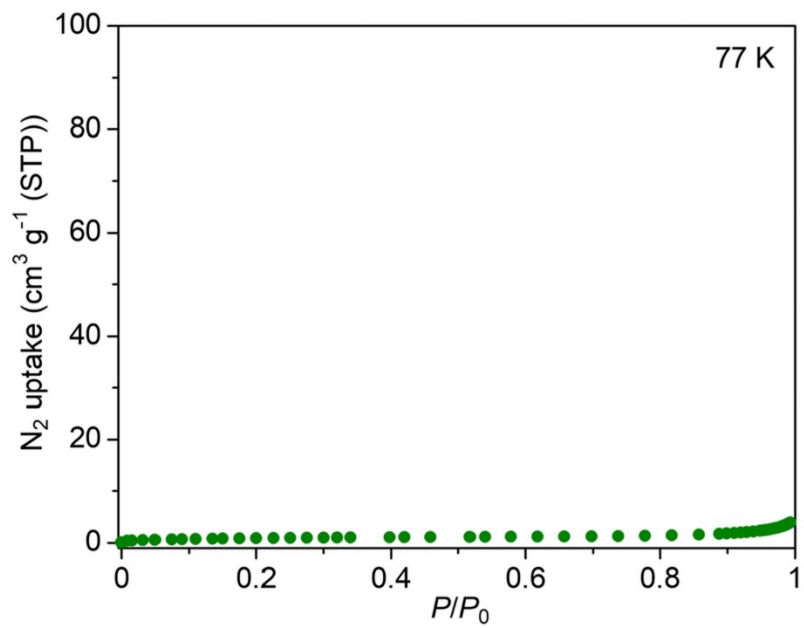


Figure S4. N₂ adsorption isotherms of MOF-688-Mg at 77 K.

Table 1. List of the activation energy (E_a) of Mg-MOF-688, estimated from Arrhenius plots of the ionic conductivity under various environmental conditions.

| Sample environment (gas or vapors) | MeCN | MeOH | EtOH | THF | N ₂ |
|---------------------------------------|------|------|------|------|----------------|
| E_a (eV) | 0.40 | 0.26 | 0.38 | 0.80 | 0.70 |