Supplementary Information

High Mg²⁺ Conduction in Three Dimensional Pores of a Metal–Organic Framework under Organic Vapors

Kouhei Aoki,[†] Kenichi Kato,[‡] Masaaki Sadakiyo*,[†]

[†]Department of Applied Chemistry, Faculty of Science Division I, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. [‡]RIKEN SPring-8 Center, Sayo-gun, Hyogo 679-5148, Japan.

E-mail: sadakiyo@rs.tus.ac.jp

Synthesis of UiO-66 (Zr₆O₄(OH)₄(bdc)₆)

The mother framework, UiO-66, was synthesized according to a previous report.¹ A mixture of ZrCl₄ (3.58 mmol, 0.834 g), 1,4-benzenedicarboxylic acid (4.67 mmol, 0.776 g), N,N-dimethylformamide (DMF, 25 mL), and hydrochloric acid (1 mL) was put in a Teflon-lined autoclave and stirred at room temperature for 1 hour. The reactor was then sealed and heated at 200 °C for 18 hours in an oven. After cooling down to room temperature, white powder was collected by centrifugation. The sample was washed with DMF (3 times) and MeOH (3 times) by repetition of centrifugation. After that, the white powder was dried at 150 °C for a night (yield: 1.22 g, 20 %).

(Ref. 1) M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp, O. K. Farha, *Chem. Commun*, 2013, **49**, 9449–9451.

Synthesis of UiO-66 \supset {Mg(TFSI)₂}_x (x \leq 2.0)

The Mg²⁺-containing MOFs, UiO-66 \supset {Mg(TFSI)₂}_x (x \leq 2.0), were prepared through impregnation method, according to previous report.² UiO-66 powder (50 mg) was immersed in ethanol solution (15 mL) of [Mg(H₂O)₆](TFSI)₂·2H₂O (8.8, 17.6, 26.4, and 35.1 mg corresponds to x = 0.5, 1.0, 1.5, and 2.0 samples, respectively.) in a test tube. The solvent was slowly evaporated by heating it at 70 °C for several days. After that, the sample was washed by 5 ml of ethanol with suction filtration and dried under the air. (Ref. 2) Y. Yoshida, K. Kato, M. Sadakiyo, *J. Phys. Chem. C*, 2021, **125**, 21124–21130.

Physical measurements

X-ray powder diffraction (XPRD) patterns were collected at room temperature using MiniFlex600 ($\lambda = 1.54059$ Å; Cu-K α) (Rigaku, Inc.). XRPD patterns under vacuum and under MeOH vapor were collected by synchrotron XRPD measurements using a sealed capillary at room temperature at the RIKEN Materials Science Beamline BL44B2 ($\lambda = 0.80000$ Å).³ The sample was sealed in a borosilicate glass capillary under vacuum at room temperature after dehydration under vacuum at 130 °C for a night, or sealed under MeOH vapor at room temperature after exposure to MeOH vapor at room temperature for 5 hours after the dehydration. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements were performed with SPS3520UV (SII Nanotechnology, Inc.). Adsorption isotherms were measured using BELSORP-max (Microtrac BEL, Inc.) and TriStar II 3020 (Micromeritics, Inc.). The samples were dried at 130 °C under vacuum for a night before the adsorption measurements.

Ionic conductivity was evaluated by Solartron 1260/1296A impedance analyzer. The pellet sample was sandwiched by porous Ag electrodes as the blocking electrodes and set inside the home-made sealed cell that is connected to a gas line. The temperature was controlled by an incubator (SU-222, Espec, Inc.). Vapor of anhydrous organic solvent was introduced into the measurement cell after the sample was preliminarily dried at 130 °C under N₂ flow for a night. Resistance value (*R*) of the sample was estimated from a simple semicircle fitting of Nyquist plots or from the real part of the impedance observed on the inflection point from the sample resistance to electrode–sample resistance. Ionic conductivity (σ) was calculated from the resistance value (*R*) using the equation, $\sigma = L/RS$, where *L* and *S* correspond to the length and area of cross section of the sample pellet, respectively. The activation energy (E_a) was calculated from the slope of the Arrhenius plots of the ionic conductivity (Arrhenius equation: $\sigma T = A\exp(-E_a/kT)$ (*T*: absolute temperature, *A*: pre-exponential factor, *k*: Boltzmann constant)).

The transport number of $Mg^{2+}(t_{Mg2+})$ was estimated by dc polarization of the sample pellet sandwiched by magnesium foils as the non-blocking electrodes. The cell, $Mg|UiO-66\supset \{Mg(TFSI)_2\}_{1.0}(MeCN)_n|Mg$, was constructed and sealed under Ar gas with MeCN vapor inside a glove bag. The dc current at the applied voltage of 0.3 V was recorded by Vertex 10A (IVIUM Technologies, Inc.) potentiostat/galvanostat at 60 °C. t_{Mg2+} was calculated by Bruce–Vincent method,⁴ according to previous report.² The resistance between the electrode and the sample was evaluated by ac impedance measurements before and after the dc polarization with Solartron 1260/1296A impedance analyzer.

(Ref. 3) K. Kato, Y. Tanaka, M. Yamauchi, K. Ohara, T. Hatsui, *J. Synchrotron Radiat.* **2019**, *26*, 762–773.

(Ref. 4) P. G. Bruce, C. A. Vincent, J. Electroanal. Chem. 1987, 225, 1–17.



Figure S1. Nyquist plots of UiO-66 \supset {Mg(TFSI)₂}_{1.0} under guest vapors or dry N₂, exemplified at 25 °C.



Figure S2. (left) Dc polarization curve of Mg|UiO-66 \supset {Mg(TFSI)₂}_{1.0}(MeCN)_{*n*}|Mg (0.3 V, 60 °C). (right) Nyquist plots of the cell before and after the polarization.

Table S1. A list of activation energy (E_a) of ionic conduction in UiO-66 \supset {Mg(TFSI)₂}_{1.0} under various vapors or dry N₂.

Vapors	MeCN	MeOH	EtOH	THF	DEC	PC	N ₂
$E_{\rm a}~({\rm eV})$	0.15	0.18	0.50	0.47	0.35	0.87	0.64



Figure S3. Synchrotron XRPD patterns of UiO-66 \supset {Mg(TFSI)₂}_{1.0} under vacuum and under MeOH vapor (after the dehydration). The intensity was normalized by the first peak (111). The lattice constants of the samples under vacuum and under MeOH vapor were calculated to be *a* = 20.7189(1) and 20.7732(1) Å (space group: Fm-3m (No. 225)), respectively, by fitting the patterns with Le bail method.



Figure S4. Adsorption isotherms of blank UiO-66 (x = 0) and UiO-66 \supset {Mg(TFSI)₂}_{1.0} (x = 1.0) for MeCN vapor.