Supporting Information

Gas Adsorption Mechanism and Kinetics of an Elastic Layer-Structured Metal-Organic Framework

Atsushi Kondo,[†*] *Natsuko Kojima,*[§] *Hiroshi Kajiro,*[‡] *Hiroshi Noguchi,*[§] *Yoshiyuki Hattori,*[¶] *Fujio Okino,*[¶] *Kazuyuki Maeda,*[†] *Tomonori Ohba,*[§] *Katsumi Kaneko,* [‖] *Hirofumi Kanoh*[§*]

[†]Department of Applied Chemistry, Tokyo University of Agriculture and Technology, 2-24-16 Koganei, Naka-cho 184-8588, Japan, [§] Graduate School of Science, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan, [‡]Nippon Steel Corporation, Shintomi, Futtsu, Chiba 293-8511, Japan, [¶] Department of Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan, [‖] Research Center for Exotic Nanocarbons (JST), Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan.

Simulation details

For Grand Canonical Monte Carlo simulation, potential parameters of ELM-11 were taken from the universal force field. Here the potential parameters of collision diameters σ and potential well depths ε are as follows. Each element is indicated by a subscript: σ_C = 0.375 nm, ε_C / k_B = 55.36 K, σ_F = 0.300 nm, ε_F / k_B = 34.22 K, σ_N = 0.325 nm, ε_N / k_B = 85.56 K, σ_{Cu} = 0.257 nm, and ε_{Cu} / k_B = 5.888 K. The partial charges of the C atoms in a bipyridine molecule are +0.09 (C_a carbon atoms), -0.030 (C_b carbon atoms) and +0.230 (C_c carbon atoms) e (Figure 1S). The partial charges of B, F, N, and Cu atoms are +0.976, -0.494, -0.490, and +2.000 e, respectively.

A three-centered Lennard-Jones potential model with three partial charges was used as CO_2 potential model. In this model, the Lennard-Jones parameters of a C atom are σ_c = 0.2753 nm and ε_c / k_b = 29.07 K, respectively, and those of an O atom are σ_o = 0.3029 nm and ε_c / k_b = 83.2 K, respectively. The partial charges of the C and O atoms in CO_2 molecules are +0.6466 and -0.3233 e, respectively. The atomic distance between C and O atoms in CO_2 molecules is 0.1143 nm.

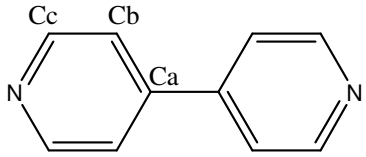


Fig 1S. Labeling of carbon atoms in a 4,4'-bipyridine molecule.

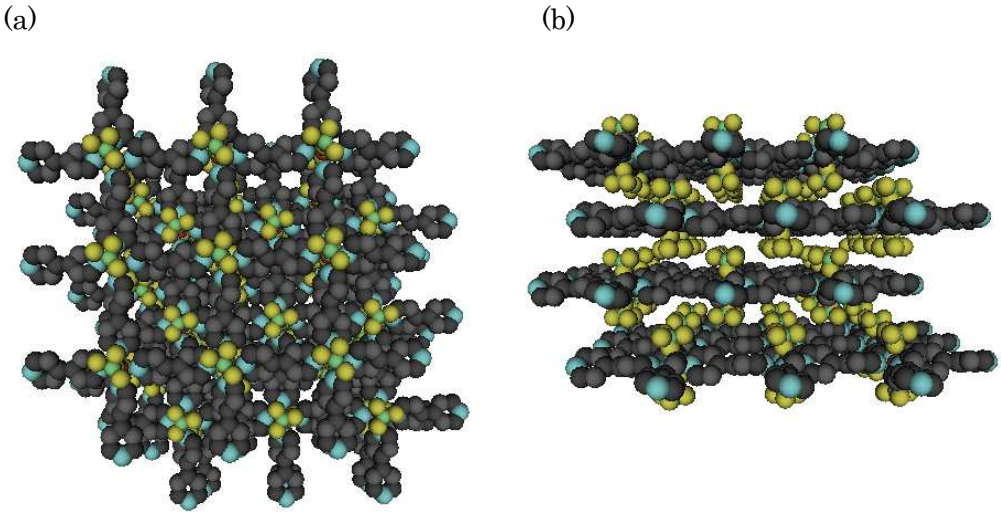
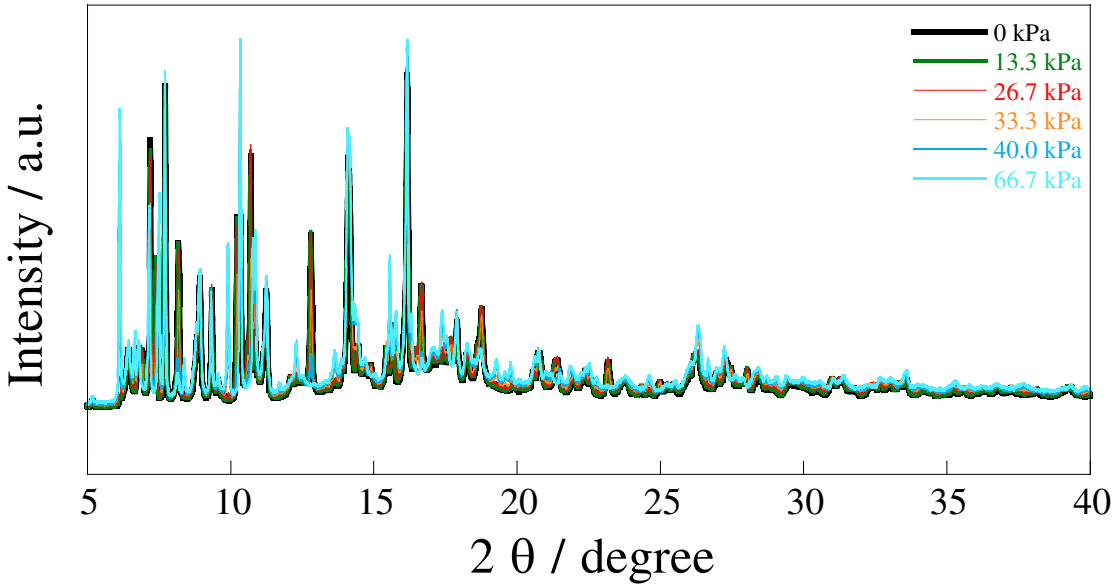
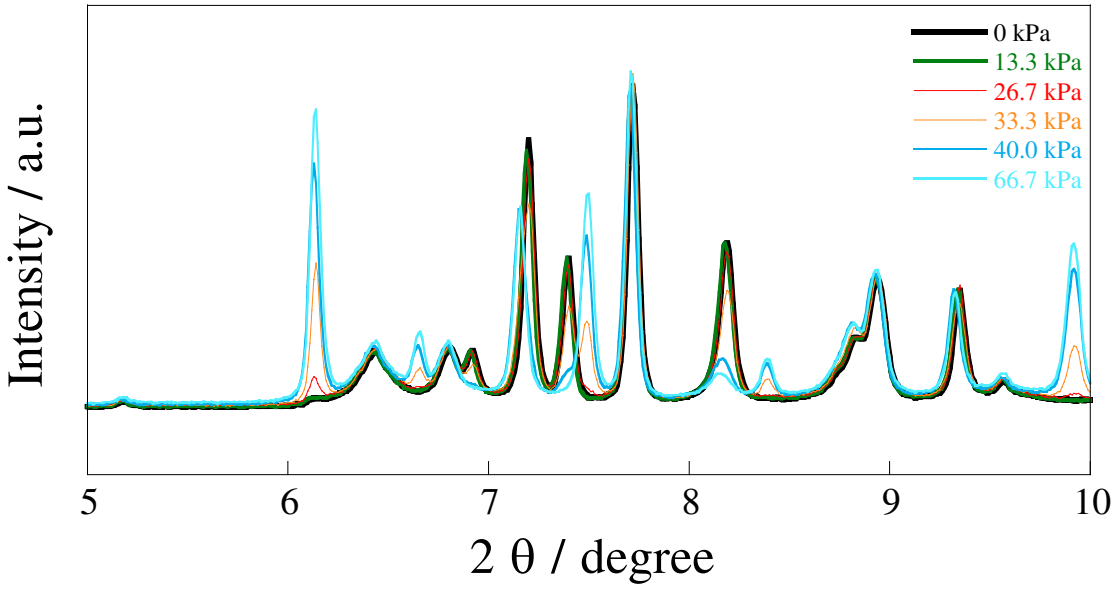


Figure 2S. Schematic representations of ELM-11 used for Grand Canonical Mote Carlo simulation. (a) Top view and (b) side view of the model. (Copper: Red, Carbon: Gray, Nitrogen: Blue, Boron: Green, Fluorine: Yellow.)

(a)


0 kPa
13.3 kPa
26.7 kPa
33.3 kPa
40.0 kPa
66.7 kPa
Intensity / a.u.
5
10
15
20
25
30
35
40
2 θ / degree

(b)


0 kPa
13.3 kPa
26.7 kPa
33.3 kPa
40.0 kPa
66.7 kPa
Intensity / a.u.
5
6
7
8
9
10
2 θ / degree

(c)

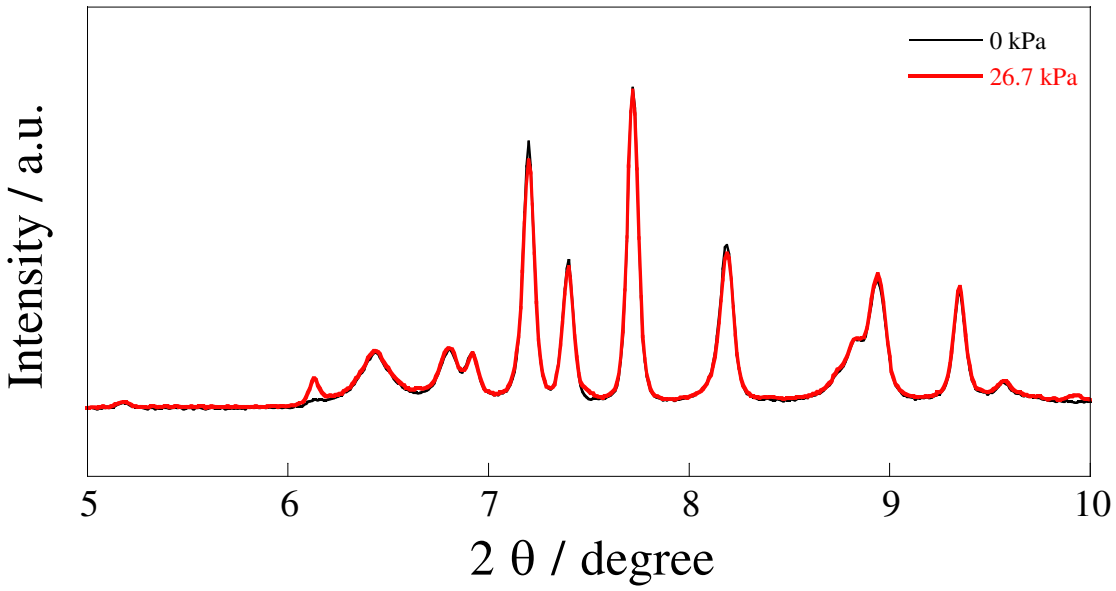


Figure 3S. In situ XRD patterns of ELM-11 at 273 K with loading CO_2 gas in the pressure range from 0 to 66.7 kPa. (a) 2θ of 5 – 40 degree, (b) 5 – 10 degree, and (c) 5 – 10 degree (Black: 0 kPa, Green: 13.3 kPa, Red: 26.7 kPa, Orange: 33.3 kPa, Blue: 40.0 kPa, Light blue: 66.7 kPa.). The gate adsorption pressure is 31 kPa.

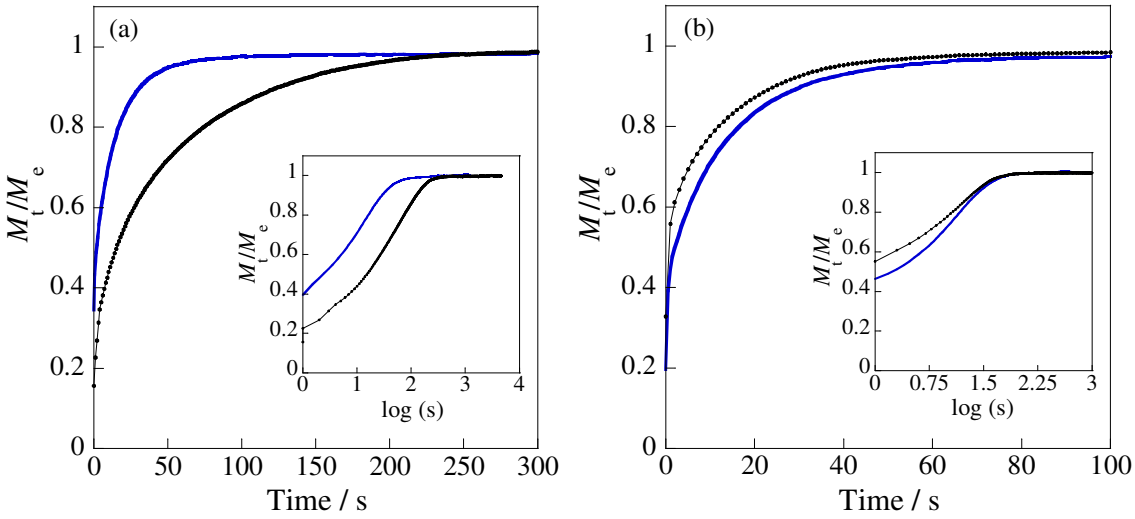
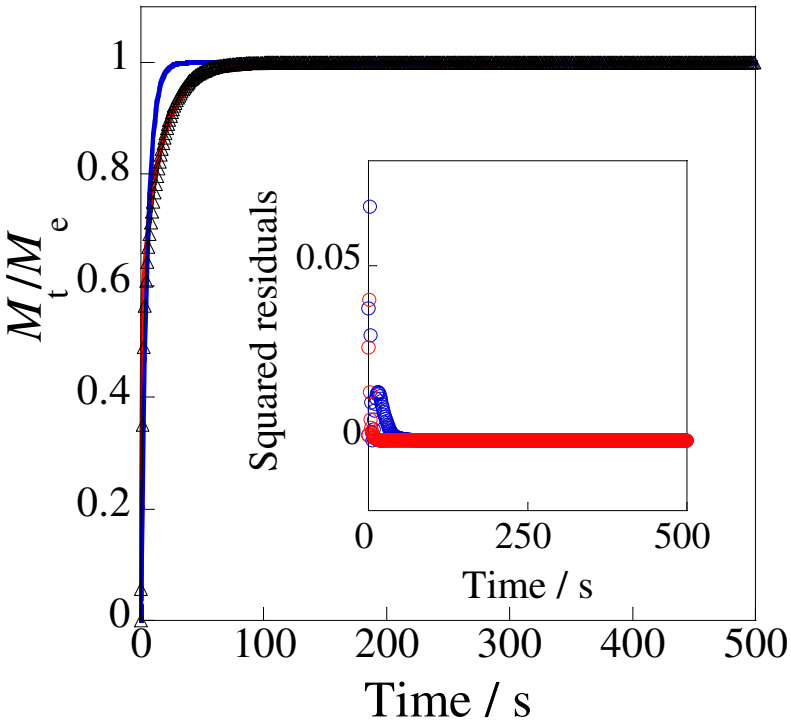
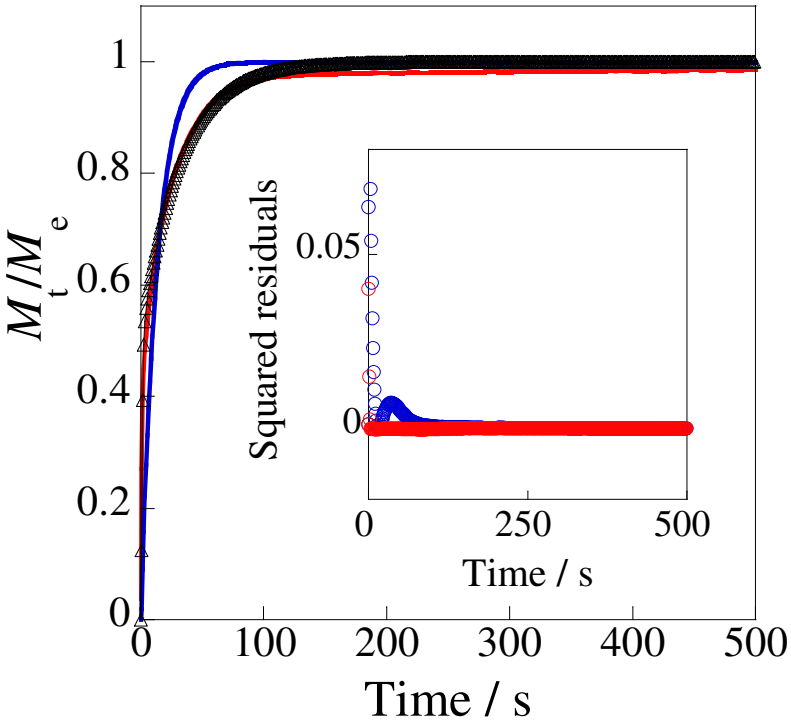


Figure 4S. Variation of *M*t/*M*e against time of ELM-11 (Black) and Zeolite 5A (Blue) (a) at 303 K and (b) 273 K. Inset: Variation of *M*t/*M*e against logarithm of time.

(a)


1
0.8
0.6
0.4
0.2
0
M_t/M_e
0
100
200
300
400
500
Time / s
Squared residuals
0.05
0
0
250
500
Time / s

(b)


1
0.8
0.6
0.4
0.2
0
M_t/M_e
0
100
200
300
400
500
Time / s
Squared residuals
0.05
0
0
250
500
Time / s

(c)

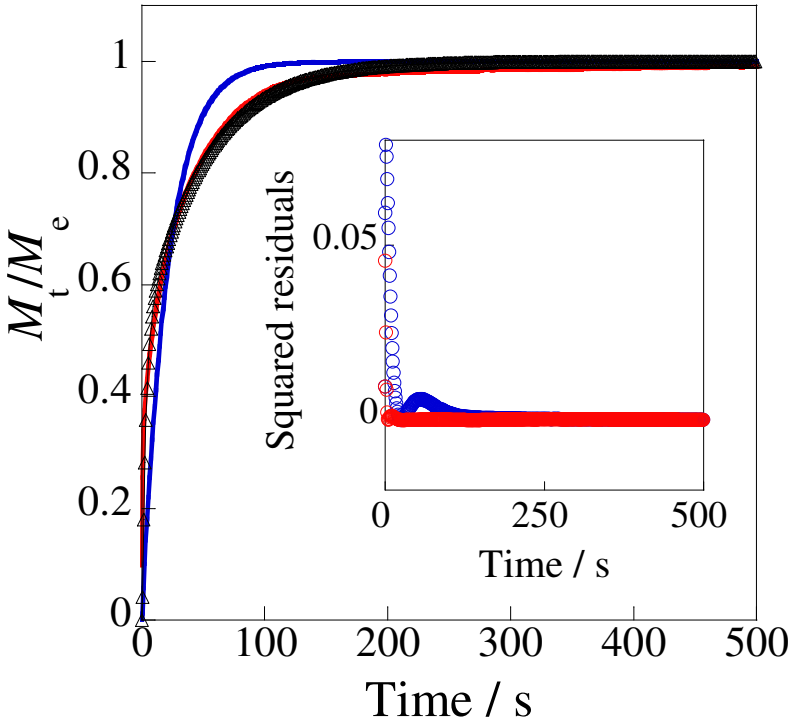


Figure 5S. Fitting results of CO_2 adsorption kinetics on ELM-11 at (a) 273 K, (b) 293 K, and (c) 298 K. Black: Experiment, red: Double exponential model, blue: Linear driving force model. Inset: Squared residuals against time.

Table 1S. Kinetics rate constants estimated by fitting the adsorption kinetic profiles to double exponential model and linear driving force model.

	Double Exponential model		Linear Driving Force model
Temperature (K)	k_1	k_2	k
273	0.87715	0.06860	0.16676
293	0.57312	0.03105	0.07168
298	0.32516	0.02041	0.04540
303	0.13923	0.01220	0.02576

Complete reference of 23

(23) Kondo, A.; Kajiro, H.; Noguchi, H.; Carlucci, L.; Proserpio, D. M.; Ciani, G.; Kato, K.; Takata, M.; Seki, H.; Sakamoto, M.; Hattori, Y.; Okino, F.; Maeda, K.; Ohba, T.; Kaneko, K.; Kanoh, H. *J. Am. Chem. Soc*. **2011**, *133*, 10512-10522.