Supporting Information

Modeling and Visualization of CO_2 adsorption on Elastic Layer-Structured Metal-Organic Framework-11: Toward a Better Understanding of Gate Adsorption Behavior

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Table S1 Crystal data for ELM-11 after gate adsorption of CO_2 at 273 K from Kondo et al.[1]

T [K]	273
$P(CO_2)$ [kPa]	98.66
formula	$CuB_2C_{20}N_4H_{16}F_8$
crystal system	monoclinic
space group	$C2/c$ (No.15)
a [nm]	1.3701
b [nm]	1.1072
c [nm]	1.8731
β [deg]	95.583
V [nm^3]	2.82797
Z	4
R_{wp}	0.13447
R_p	0.07536

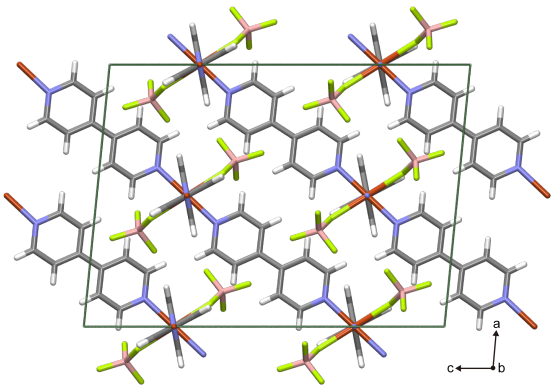

Figure S1. Framework structure of ELM-11 after gate adsorption of CO_2 at 273 K from Kondo et al.[1]

Table S2 Interaction parameters from the UFF and atomic charges from Mulliken population analysis. Atom types are shown in Figure S2

Atom	σ_{UFF} [nm]	ε_{UFF} / k_B [K]	q [e]
Cu	0.3114	2.517	0.611
B	0.3638	90.623	0.744
F1	0.2997	25.173	–0.405
F2	0.2997	25.173	–0.409
F3	0.2997	25.173	–0.385
F4	0.2997	25.173	–0.378
N1	0.3261	34.739	–0.486
N2	0.3261	34.739	–0.428
N3	0.3261	34.739	–0.438
C1	0.3431	52.863	0.124
C2	0.3431	52.863	–0.046
C3	0.3431	52.863	0.081
C4	0.3431	52.863	–0.089
C5	0.3431	52.863	0.098
C6	0.3431	52.863	0.214
C7	0.3431	52.863	–0.065
C8	0.3431	52.863	–0.007
C9	0.3431	52.863	0.033
C10	0.3431	52.863	–0.065
C11	0.3431	52.863	0.167
H1	0.2571	22.152	0.086
H2	0.2571	22.152	0.217
H3	0.2571	22.152	0.142
H4	0.2571	22.152	0.121
H5	0.2571	22.152	0.126
H6	0.2571	22.152	0.105
H7	0.2571	22.152	0.108
H8	0.2571	22.152	0.111

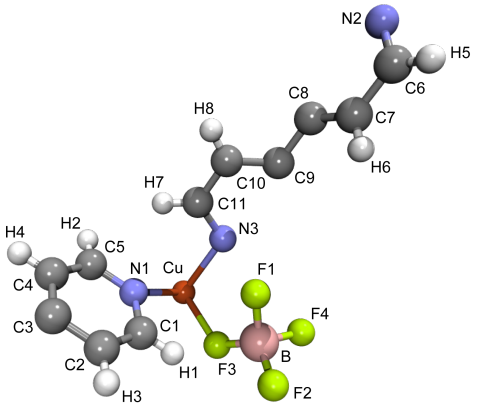

Figure S2 Atom types in the ELM-11 framework.

Table S3 Interaction parameters for CO_2 molecule

site C	
σ_{gg} [nm]	0.2789
ε_{gg} / k_B [K]	29.66
q [e]	+0.576
site O	
σ_{gg} [nm]	0.3011
ε_{gg} / k_B [K]	82.96
q [e]	–0.288
$r_{C\text{-}O}$ [nm]	0.118
$\theta_{\angle OCO}$ [deg]	180

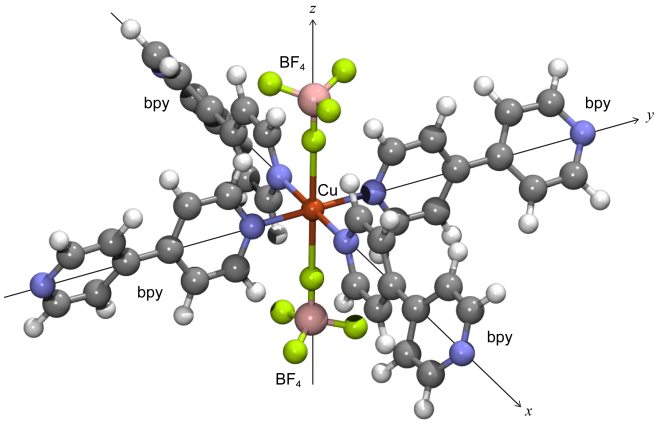

Figure S3 Isolated fragment of ELM-11 ($Cu(BF_4)_2(bpy)_4$) used for the DFT calculations.

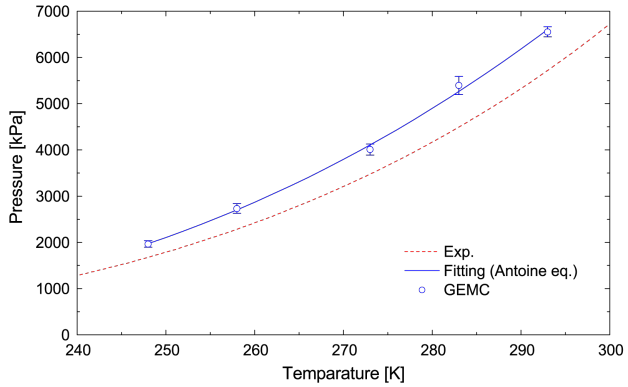

Figure S4 A comparison of the saturated vapor pressure–temperature curves of CO_2 from the GEMC simulations and experiment.

$$\ln P\,[\mathrm{Pa}] = A - \frac{B}{C + T\,[\mathrm{K}]}$$

$A = 20.8239$, $B = 1206.63$, $C = -57.356$

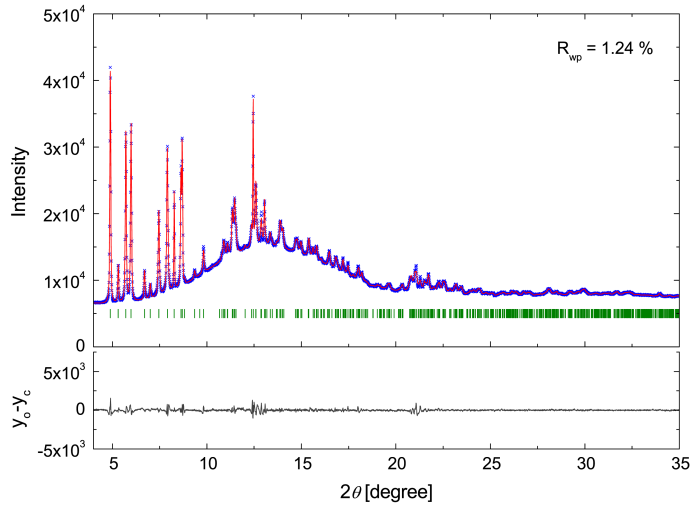

Figure S5 Le Bail fitting for the XRPD pattern of ELM-11 ⊃ 2CO_2 at P/P_0 = 0.0286 and 273 K. The bottom panel shows the residual error.

Table S4 Crystal data for ELM-11 ⊃ 2CO_2 obtained by the Le Bail method

T [K]	273
$P(CO_2)$ [kPa]	100
crystal system	monoclinic
space group	$C2/c$ (No. 15)
a [nm]	1.36850
b [nm]	1.10487
c [nm]	1.87153
β [deg]	95.6635
V [nm^3]	2.81597
R_{wp}	0.01236
R_p	0.00825
R_I	0.01075
S	1.2562

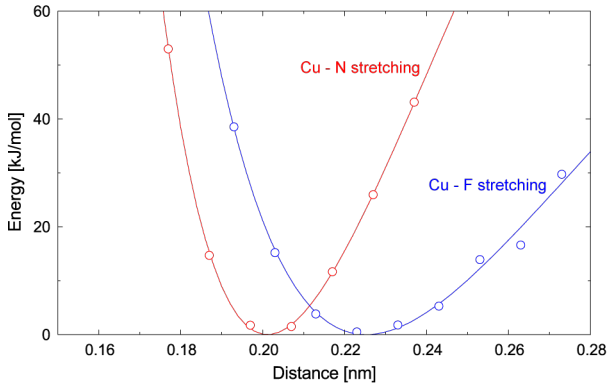

Figure S6 Bonded potentials [bond stretching (Cu–N and Cu–F)] determined by the DFT calculations for the $Cu(BF_4)_2(bpy)_4$ cluster.

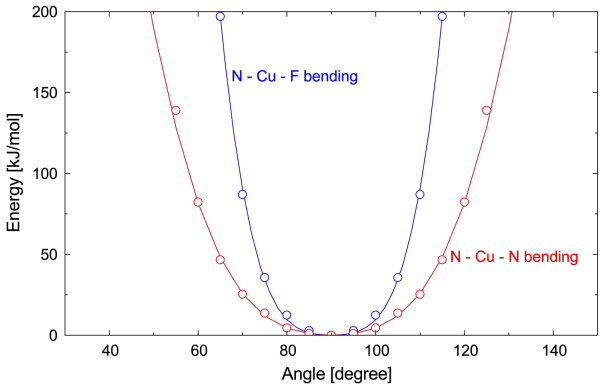

Figure S7 Bonded potentials [angle bending (N–Cu–N and N–Cu–F)] determined by the DFT calculations for the $Cu(BF_4)_2(bpy)_4$ cluster.

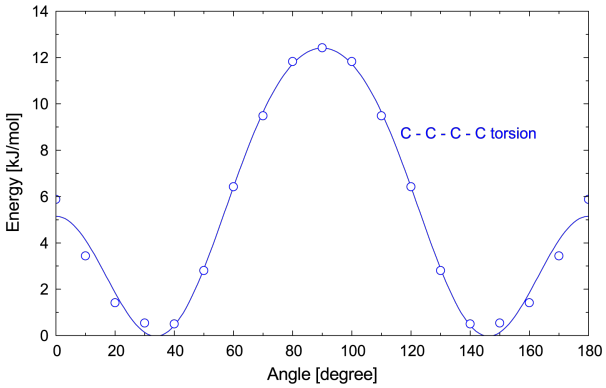

Figure S8 Bonded potential [bond rotation between the pyridine rings of bpy (C–C–C–C)] determined by the DFT calculations for the isolated bpy molecule.

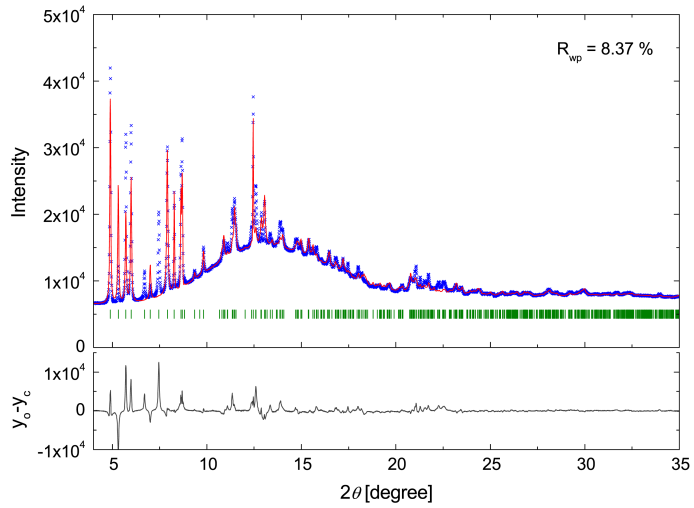

Figure S9 Rietveld refinement pattern of ELM-11 ⊃ $2CO_2$ at P/P_0 = 0.0286 and 273 K obtained using **2A** ⊃ $2CO_2$ as a starting structure. Only the parameters of the profile function were refined. The bottom panel shows the residual error.

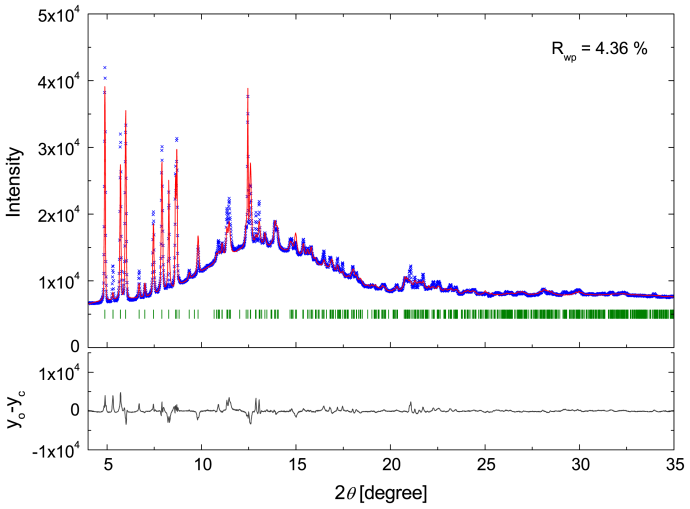

Figure S10 Rietveld refinement pattern of ELM-11 ⊃ $2CO_2$ at P/P_0 = 0.0286 and 273 K obtained using **2B** ⊃ $2CO_2$ as a starting structure. Only the parameters of the profile function were refined. The bottom panel shows the residual error.

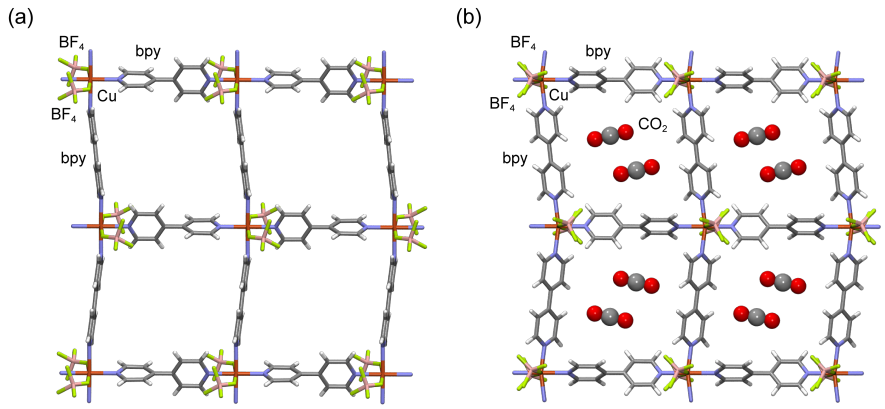

Figure S11 (a) Framework structure of ELM-11 from Kondo et al.[1] and (b) Rietveld refined structure of ELM-11 ⊃ $2CO_2$ in this study.

Table S5 Atomic coordinates of ELM-11 ⊃ $2CO_2$ in space group C2/*c*. Atom types of ELM-11 are shown in Figure S2 and C12, O1, and O2 are atoms of adsorbed CO_2

Atom	*x*	*y*	*z*	σ_x†	σ_y†	σ_z†	*U* [nm^2] †
Cu	0	0.19152	0.75000	–	0.00125	–	1.18×10^{-4}
B	0.19250	0.12742	0.63958	0.00693	0.00694	0.00590	1.04×10^{-3}
F1	0.27016	0.07259	0.68372	0.00218	0.00282	0.00142	1.04×10^{-3}
F2	0.22999	0.21848	0.59849	0.00242	0.00236	0.00161	1.04×10^{-3}
F3	0.12260	0.17925	0.68394	0.00247	0.00333	0.00166	2.46×10^{-4}
F4	0.14644	0.03989	0.59428	0.00201	0.00279	0.00192	1.04×10^{-3}
N1	0.09679	0.21443	0.84176	0.00283	0.00388	0.00189	1.27×10^{-4}
N2	0	0.37854	0.75000	–	0.00569	–	1.27×10^{-4}
N3	0	0.00896	0.75000	–	0.00653	–	1.27×10^{-4}
C1	0.17776	0.28272	0.84217	0.00385	0.00514	0.00264	1.27×10^{-4}
C2	0.23850	0.29858	0.90538	0.00336	0.00446	0.00283	1.27×10^{-4}
C3	0.21711	0.24235	0.96597	0.00386	0.00494	0.00266	1.27×10^{-4}
C4	0.13669	0.17043	0.96583	0.00378	0.00496	0.00282	1.27×10^{-4}
C5	0.07549	0.15655	0.90228	0.00404	0.00447	0.00299	1.27×10^{-4}
C6	0.04336	0.44167	0.69548	0.00298	0.00451	0.00258	1.27×10^{-4}
C7	0.04291	0.56803	0.69603	0.00288	0.00396	0.00239	1.27×10^{-4}
C8	0	0.63069	0.75000	–	0.00610	–	1.27×10^{-4}
C9	0	0.75805	0.75000	–	0.00546	–	1.27×10^{-4}
C10	0.08640	0.82163	0.76656	0.00329	0.00389	0.00249	1.27×10^{-4}
C11	0.08550	0.94772	0.76643	0.00324	0.00367	0.00242	1.27×10^{-4}
H1	0.19580	0.32551	0.79322	–	–	–	1.27×10^{-4}
H2	0.12035	0.12460	1.00428	–	–	–	1.27×10^{-4}
H3	0.30071	0.35575	0.90610	–	–	–	1.27×10^{-4}
H4	0.01106	0.09969	0.90019	–	–	–	1.27×10^{-4}
H5	0.07637	0.39278	0.65398	–	–	–	1.27×10^{-4}
H6	0.07574	0.61762	0.65472	–	–	–	1.27×10^{-4}
H7	0.15300	0.99740	0.77937	–	–	–	1.27×10^{-4}
H8	0.15459	0.77345	0.77962	–	–	–	1.27×10^{-4}
C12	0.39463	0.16086	0.51660	0.01258	0.00653	0.00905	4.45×10^{-3}
O1	0.40552	0.26500	0.52888	0.00558	0.00414	0.00427	4.45×10^{-3}
O2	0.38373	0.05662	0.50429	0.00516	0.00510	0.00394	4.45×10^{-3}

† σ_x, σ_y and σ_z are standard deviations and *U* is isotropic atomic displacement parameter. The *U* parameters for carbon and hydrogen atoms of the ELM-11 framework were fixed during the Rietveld refinement. The *U* parameters for CO_2 (C12, O1, and O2) are those evaluated from anisotropic atomic displacement parameters (see Table S6) and the lattice parameters.

Table S6 Anisotropic atomic displacement parameters of adsorbed CO_2 on ELM-11

Atom	U_{11} [nm^2]	U_{22} [nm^2]	U_{33} [nm^2]	U_{12} [nm^2]	U_{13} [nm^2]	U_{23} [nm^2]
C12	2.09×10^{-3}	7.96×10^{-3}	3.42×10^{-3}	-1.35×10^{-3}	8.22×10^{-4}	6.75×10^{-4}
O1	2.09×10^{-3}	7.96×10^{-3}	3.42×10^{-3}	-1.35×10^{-3}	8.22×10^{-4}	6.75×10^{-4}
O2	2.09×10^{-3}	7.96×10^{-3}	3.42×10^{-3}	-1.35×10^{-3}	8.22×10^{-4}	6.75×10^{-4}

Table S7 Atomic charges from Mulliken population analysis. Atom types are shown in Figure S2

Atom	q [e]
Cu	0.615
B	0.774
F1	–0.408
F2	–0.368
F3	–0.421
F4	–0.399
N1	–0.382
N2	–0.465
N3	–0.409
C1	0.088
C2	–0.120
C3	0.046
C4	–0.046
C5	0.052
C6	0.106
C7	–0.073
C8	0.077
C9	0.038
C10	–0.118
C11	0.098
H1	0.147
H2	0.181
H3	0.161
H4	0.128
H5	0.169
H6	0.122
H7	0.154
H8	0.183

Reference

1.Kondo, A.; Noguchi, H.; Ohnishi, S.; Kajiro, H.; Tohdoh, A.; Hattori, Y.; Xu, W.-C.; Tanaka, H.; Kanoh, H.; Kaneko, K. *Nano Lett.* **2006**, *6*, 2581.