Electronic Supplementary Information

Understanding gate adsorption behaviour of CO_2 on elastic layer-structured metal-organic framework-11

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§1 Supplementary figures and tables

Table S1 Interaction parameters for a CO_2 molecule[1]

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
The C–O bond length [nm]	0.118
The O–C–O bond angle [deg]	180

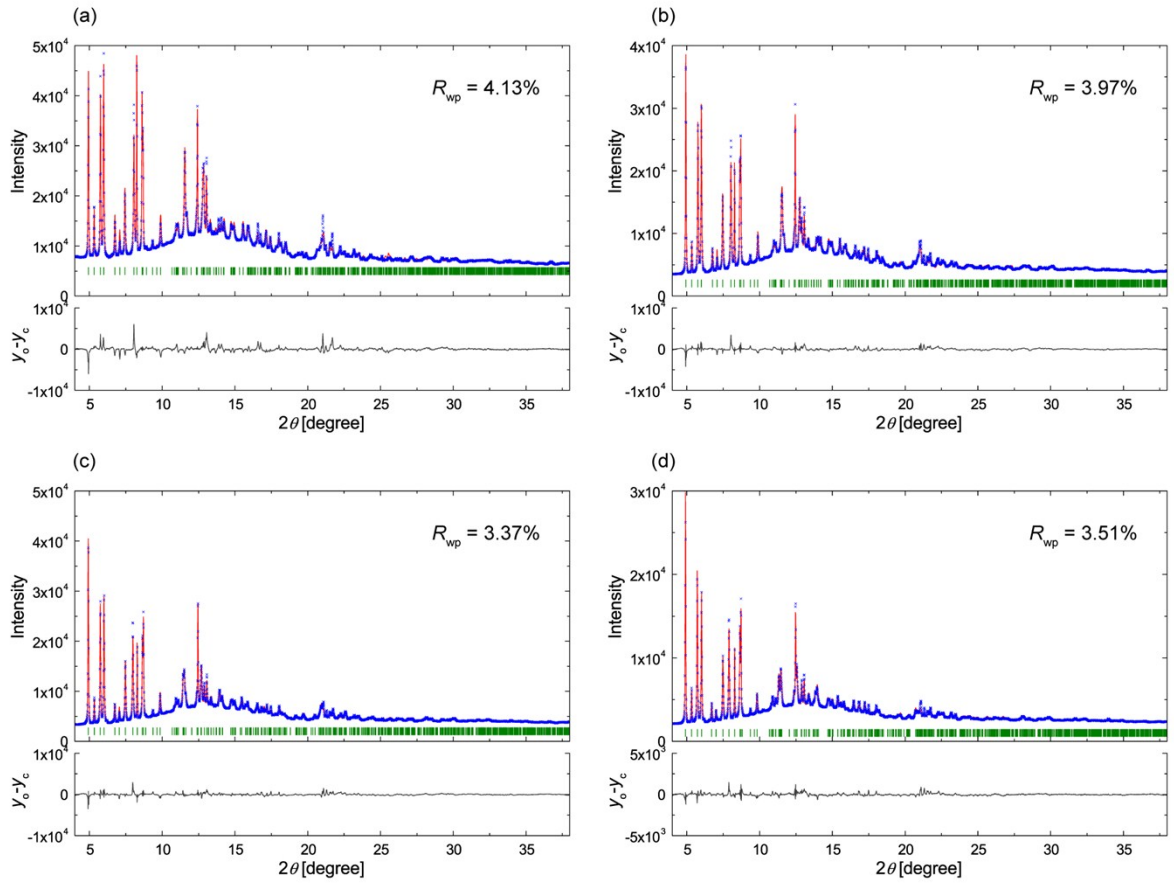

Fig. S1 Rietveld refinement XRPD patterns of ELM-11 ⊃ $2CO_2$ at (a) 195 K, (b) 223 K, (c) 248 K, and (d) 298 K. The bottom panels show the residual error.

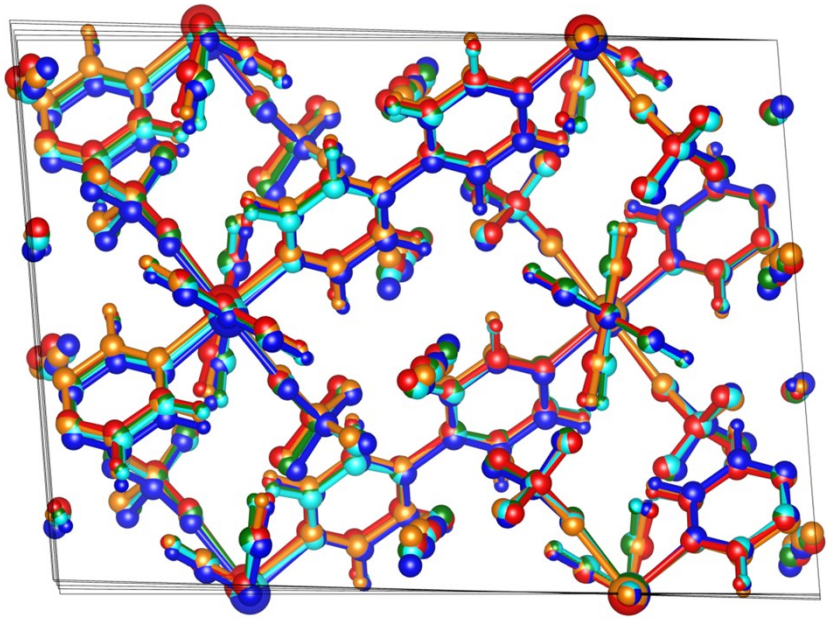

Fig. S2 Snapshot of ELM-11 ⊃ $2CO_2$ at 195 K (blue), 223 K (cyan), 248 K (green), 273 K (orange), and (d) 298 K (red).

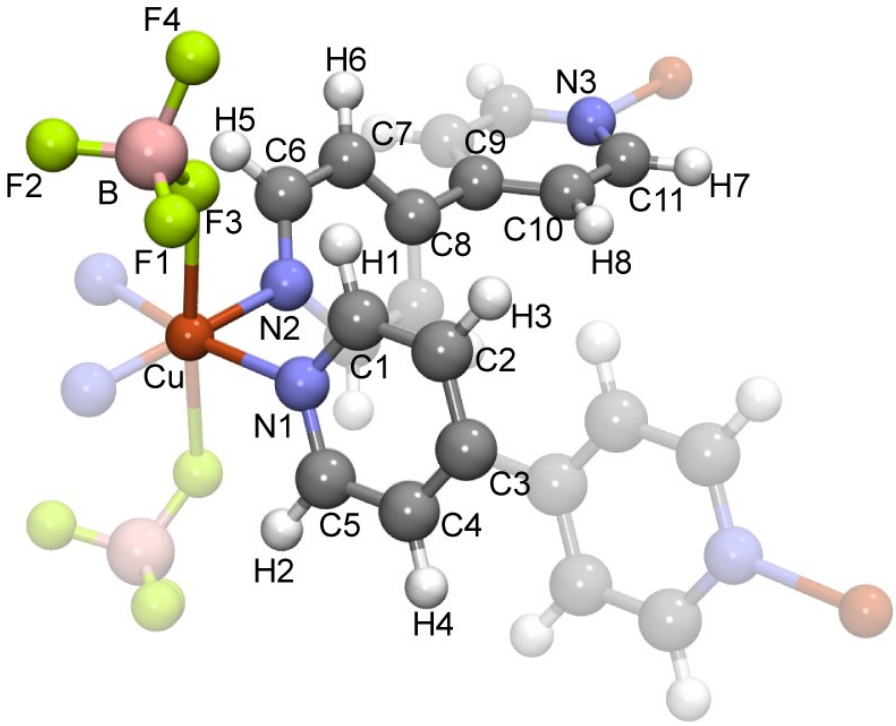

Fig. S3 Atom types in the ELM-11 framework.

Table S2 Atomic coordinates of ELM-11 ⊃ $2CO_2$ at 195 K in space group $C2/c$. Atom types of ELM-11 are shown in Fig. S3 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	0.19975	0.75	–	0.00163	–	7.07×10^{-5}
B	0.19324	0.13481	0.63340	0.00618	0.00579	0.00442	2.83×10^{-4}
F1	0.27593	0.08389	0.67688	0.00202	0.00255	0.00147	2.83×10^{-4}
F2	0.22855	0.21220	0.58290	0.00203	0.00242	0.00139	2.83×10^{-4}
F3	0.12945	0.20055	0.67972	0.00204	0.00291	0.00149	2.83×10^{-4}
F4	0.13921	0.03984	0.59684	0.00205	0.00283	0.00171	2.83×10^{-4}
N1	0.10185	0.20157	0.84166	0.00342	0.00542	0.00249	2.83×10^{-4}
N2	0	0.38282	0.75	–	0.00825	–	2.83×10^{-4}
N3	0	0.01394	0.75	–	0.00774	–	2.83×10^{-4}
C1	0.18136	0.27543	0.84330	0.00514	0.00557	0.00302	2.83×10^{-4}
C2	0.24022	0.29421	0.90694	0.00420	0.00537	0.00411	2.83×10^{-4}
C3	0.21803	0.23948	0.96591	0.00485	0.00560	0.00285	2.83×10^{-4}
C4	0.13988	0.16599	0.96523	0.00503	0.00531	0.00340	2.83×10^{-4}
C5	0.08072	0.14675	0.90163	0.00419	0.00501	0.00400	2.83×10^{-4}
C6	0.04097	0.44332	0.69588	0.00351	0.00481	0.00302	2.83×10^{-4}
C7	0.04201	0.56587	0.69463	0.00347	0.00481	0.00329	2.83×10^{-4}
C8	0	0.63035	0.75	–	0.00837	–	2.83×10^{-4}
C9	0	0.76477	0.75	–	0.00720	–	2.83×10^{-4}
C10	0.08853	0.82973	0.76799	0.00358	0.00480	0.00294	2.83×10^{-4}
C11	0.08627	0.95315	0.76747	0.00333	0.00506	0.00261	2.83×10^{-4}
H1	0.19880	0.32009	0.79417	–	–	–	4.24×10^{-4}
H2	0.12278	0.12142	1.01447	–	–	–	4.24×10^{-4}
H3	0.30363	0.35319	0.90805	–	–	–	4.24×10^{-4}
H4	0.01773	0.08720	0.90126	–	–	–	4.24×10^{-4}
H5	0.07284	0.39288	0.65367	–	–	–	4.24×10^{-4}
H6	0.07483	0.61283	0.65148	–	–	–	4.24×10^{-4}
H7	0.15312	1.00378	0.78095	–	–	–	4.24×10^{-4}
H8	0.15713	0.78296	0.78197	–	–	–	4.24×10^{-4}
C12	0.41480	0.17871	0.51775	0.00979	0.01063	0.00771	2.54×10^{-3}
O1	0.44862	0.27429	0.53614	0.00569	0.00611	0.00322	2.54×10^{-3}
O2	0.37952	0.08370	0.49942	0.00495	0.00679	0.00323	2.54×10^{-3}

σ_x, σ_y and σ_z are standard deviations and U is isotropic atomic displacement parameter. The U parameters for CO_2 (C12, O1, and O2) are those evaluated from anisotropic atomic displacement parameters ($U_{11} = 2.80 \times 10^{-3}$ nm^2, $U_{22} = 3.79 \times 10^{-3}$ nm^2, $U_{33} = 1.04 \times 10^{-3}$ nm^2, $U_{12} = -2.84 \times 10^{-4}$ nm^2, $U_{13} = 1.66 \times 10^{-4}$ nm^2, and $U_{23} = 1.00 \times 10^{-5}$ nm^2). The linear constraints for the atomic displacement parameters were imposed as follows: $U^{B} = U^{F} = U^{N} = U^{C(host)}$; $U^{Cu} = 0.25 \times U^{B}$; $U^{H} = 1.5 \times U^{B}$; and $U_{ij}^{C12} = U_{ij}^{O}$.

Table S3 Atomic coordinates of ELM-11 ⊃ $2CO_2$ at 223 K in space group *C*2/*c*. Atom types of ELM-11 are shown in Fig. S3 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	0.19971	0.75	–	0.00134	–	7.97×10^{-5}
B	0.19498	0.12291	0.63928	0.00521	0.00549	0.00400	3.19×10^{-4}
F1	0.27064	0.07080	0.68430	0.00183	0.00222	0.00116	3.19×10^{-4}
F2	0.23645	0.20722	0.59312	0.00153	0.00240	0.00128	3.19×10^{-4}
F3	0.12661	0.18392	0.68249	0.00199	0.00255	0.00131	3.19×10^{-4}
F4	0.14537	0.03097	0.59753	0.00177	0.00239	0.00145	3.19×10^{-4}
N1	0.09473	0.20572	0.84092	0.00278	0.00441	0.00233	3.19×10^{-4}
N2	0	0.38118	0.75	–	0.00641	–	3.19×10^{-4}
N3	0	0.01191	0.75	–	0.00672	–	3.19×10^{-4}
C1	0.16828	0.28755	0.84029	0.00413	0.00549	0.00234	3.19×10^{-4}
C2	0.23008	0.30567	0.90284	0.00339	0.00477	0.00316	3.19×10^{-4}
C3	0.21463	0.23989	0.96364	0.00386	0.00451	0.00269	3.19×10^{-4}
C4	0.14055	0.15900	0.96229	0.00417	0.00421	0.00329	3.19×10^{-4}
C5	0.08087	0.14241	0.90066	0.00404	0.00418	0.00366	3.19×10^{-4}
C6	0.04461	0.44180	0.69798	0.00308	0.00455	0.00258	3.19×10^{-4}
C7	0.04528	0.56463	0.69710	0.00324	0.00388	0.00308	3.19×10^{-4}
C8	0	0.62857	0.75	–	0.00802	–	3.19×10^{-4}
C9	0	0.76208	0.75	–	0.00610	–	3.19×10^{-4}
C10	0.08865	0.82615	0.75975	0.00337	0.00412	0.00242	3.19×10^{-4}
C11	0.08725	0.95127	0.75965	0.00326	0.00440	0.00231	3.19×10^{-4}
H1	0.17959	0.33867	0.79219	–	–	–	4.78×10^{-4}
H2	0.12840	0.10727	1.00999	–	–	–	4.78×10^{-4}
H3	0.28967	0.37053	0.90402	–	–	–	4.78×10^{-4}
H4	0.02165	0.07714	0.90029	–	–	–	4.78×10^{-4}
H5	0.07960	0.39173	0.65726	–	–	–	4.78×10^{-4}
H6	0.08072	0.61226	0.65563	–	–	–	4.78×10^{-4}
H7	0.15564	1.00128	0.76728	–	–	–	4.78×10^{-4}
H8	0.15816	0.77847	0.76734	–	–	–	4.78×10^{-4}
C12	0.39776	0.15554	0.51205	0.01526	0.01581	0.01358	2.73×10^{-3}
O1	0.42726	0.25116	0.53226	0.01365	0.01030	0.00964	2.73×10^{-3}
O2	0.36826	0.05991	0.49183	0.01173	0.01234	0.00894	2.73×10^{-3}

σ_x, σ_y and σ_z are standard deviations and U is isotropic atomic displacement parameter. The U parameters for CO_2 (C12, O1, and O2) are those evaluated from anisotropic atomic displacement parameters ($U_{11} = 2.74 \times 10^{-3}$ nm^2, $U_{22} = 3.95 \times 10^{-3}$ nm^2, $U_{33} = 1.63 \times 10^{-3}$ nm^2, $U_{12} = -6.02 \times 10^{-4}$ nm^2, $U_{13} = 9.37 \times 10^{-4}$ nm^2, and $U_{23} = 7.84 \times 10^{-4}$ nm^2). The linear constraints for the atomic displacement parameters were imposed as follows: $U^{B} = U^{F} = U^{N} = U^{C(host)}$; $U^{Cu} = 0.25 \times U^{B}$; $U^{H} = 1.5 \times U^{B}$; and $U_{ij}^{C12} = U_{ij}^{O}$.

Table S4 Atomic coordinates of ELM-11 ⊃ $2CO_2$ at 248 K in space group $C2/c$. Atom types of ELM-11 are shown in Fig. S3 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	0.19491	0.75	–	0.00130	–	9.30×10^{-5}
B	0.19698	0.12616	0.64006	0.00603	0.00564	0.00405	3.72×10^{-4}
F1	0.27646	0.07926	0.68384	0.00186	0.00224	0.00114	3.72×10^{-4}
F2	0.23268	0.20228	0.58870	0.00156	0.00235	0.00121	3.72×10^{-4}
F3	0.13342	0.19372	0.68351	0.00189	0.00282	0.00133	3.72×10^{-4}
F4	0.14370	0.02899	0.60492	0.00163	0.00257	0.00142	3.72×10^{-4}
N1	0.09572	0.20417	0.84045	0.00282	0.00433	0.00231	3.72×10^{-4}
N2	0	0.38058	0.75	–	0.00660	–	3.72×10^{-4}
N3	0	0.01218	0.75	–	0.00712	–	3.72×10^{-4}
C1	0.16923	0.28574	0.84068	0.00411	0.00564	0.00252	3.72×10^{-4}
C2	0.23009	0.30392	0.90320	0.00338	0.00518	0.00316	3.72×10^{-4}
C3	0.21446	0.23936	0.96315	0.00399	0.00469	0.00277	3.72×10^{-4}
C4	0.14060	0.15836	0.96160	0.00450	0.00498	0.00301	3.72×10^{-4}
C5	0.08103	0.14087	0.89977	0.00387	0.00428	0.00381	3.72×10^{-4}
C6	0.04430	0.44123	0.69820	0.00297	0.00468	0.00271	3.72×10^{-4}
C7	0.04495	0.56407	0.69735	0.00333	0.00411	0.00306	3.72×10^{-4}
C8	0	0.62806	0.75	–	0.00785	–	3.72×10^{-4}
C9	0	0.76162	0.75	–	0.00637	–	3.72×10^{-4}
C10	0.08849	0.82572	0.75979	0.00334	0.00438	0.00232	3.72×10^{-4}
C11	0.08713	0.95155	0.75970	0.00349	0.00396	0.00254	3.72×10^{-4}
H1	0.18092	0.33668	0.79276	–	–	–	5.58×10^{-4}
H2	0.12851	0.10718	1.00935	–	–	–	5.58×10^{-4}
H3	0.28961	0.36872	0.90467	–	–	–	5.58×10^{-4}
H4	0.02180	0.07571	0.89870	–	–	–	5.58×10^{-4}
H5	0.07905	0.39119	0.65764	–	–	–	5.58×10^{-4}
H6	0.08012	0.61177	0.65608	–	–	–	5.58×10^{-4}
H7	0.15542	1.00155	0.76736	–	–	–	5.58×10^{-4}
H8	0.15785	0.77798	0.76742	–	–	–	5.58×10^{-4}
C12	0.39786	0.15370	0.51125	0.01634	0.02360	0.01665	3.27×10^{-3}
O1	0.42876	0.24739	0.53383	0.01721	0.01727	0.01316	3.27×10^{-3}
O2	0.36696	0.06002	0.48869	0.01518	0.01865	0.01237	3.27×10^{-3}

σ_x, σ_y and σ_z are standard deviations and U is isotropic atomic displacement parameter. The U parameters for CO_2 (C12, O1, and O2) are those evaluated from anisotropic atomic displacement parameters ($U_{11} = 2.33 \times 10^{-3}$ nm^2, $U_{22} = 5.79 \times 10^{-3}$ nm^2, $U_{33} = 1.70 \times 10^{-3}$ nm^2, $U_{12} = 6.41 \times 10^{-4}$ nm^2, $U_{13} = 2.95 \times 10^{-4}$ nm^2, and $U_{23} = 1.59 \times 10^{-3}$ nm^2). The linear constraints for the atomic displacement parameters were imposed as follows: $U^{B} = U^{F} = U^{N} = U^{C(host)}$; $U^{Cu} = 0.25 \times U^{B}$; $U^{H} = 1.5 \times U^{B}$; and $U_{ij}^{C12} = U_{ij}^{O}$.

Table S5 Atomic coordinates of ELM-11 ⊃ $2CO_2$ at 298 K in space group $C2/c$. Atom types of ELM-11 are shown in Fig. S3 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	0.19281	0.75	–	0.00114	–	1.34×10^{-4}
B	0.19563	0.11984	0.64423	0.00569	0.00515	0.00422	5.34×10^{-4}
F1	0.27073	0.06941	0.69054	0.00161	0.00190	0.00123	5.34×10^{-4}
F2	0.23654	0.19253	0.59436	0.00152	0.00286	0.00114	5.34×10^{-4}
F3	0.13256	0.19178	0.68463	0.00205	0.00255	0.00127	5.34×10^{-4}
F4	0.14045	0.02442	0.60743	0.00159	0.00234	0.00131	5.34×10^{-4}
N1	0.09943	0.19919	0.83834	0.00257	0.00436	0.00200	5.34×10^{-4}
N2	0	0.38035	0.75	–	0.00586	–	5.34×10^{-4}
N3	0	0.01305	0.75	–	0.00674	–	5.34×10^{-4}
C1	0.17252	0.27971	0.84012	0.00376	0.00549	0.00264	5.34×10^{-4}
C2	0.23247	0.30018	0.90425	0.00310	0.00506	0.00283	5.34×10^{-4}
C3	0.21649	0.23863	0.96391	0.00366	0.00499	0.00261	5.34×10^{-4}
C4	0.14311	0.15790	0.96174	0.00373	0.00448	0.00265	5.34×10^{-4}
C5	0.08398	0.13864	0.89771	0.00382	0.00377	0.00329	5.34×10^{-4}
C6	0.04017	0.44108	0.69691	0.00267	0.00371	0.00257	5.34×10^{-4}
C7	0.04084	0.56606	0.69588	0.00315	0.00380	0.00263	5.34×10^{-4}
C8	0	0.62901	0.75	–	0.00730	–	5.34×10^{-4}
C9	0	0.76257	0.75	–	0.00598	–	5.34×10^{-4}
C10	0.08639	0.82586	0.77173	0.00332	0.00385	0.00262	5.34×10^{-4}
C11	0.08469	0.95217	0.77137	0.00323	0.00404	0.00240	5.34×10^{-4}
H1	0.18536	0.32892	0.79222	–	–	–	8.01×10^{-4}
H2	0.12980	0.10800	1.00929	–	–	–	8.01×10^{-4}
H3	0.29137	0.36522	0.90578	–	–	–	8.01×10^{-4}
H4	0.02503	0.07370	0.89658	–	–	–	8.01×10^{-4}
H5	0.07159	0.39088	0.65549	–	–	–	8.01×10^{-4}
H6	0.07267	0.61354	0.65360	–	–	–	8.01×10^{-4}
H7	0.15060	1.00245	0.78805	–	–	–	8.01×10^{-4}
H8	0.15366	0.77845	0.78860	–	–	–	8.01×10^{-4}
C12	0.39657	0.14921	0.50408	0.01687	0.01628	0.01854	3.64×10^{-3}
O1	0.42000	0.24763	0.52335	0.01413	0.00948	0.01445	3.64×10^{-3}
O2	0.37298	0.05091	0.48479	0.01173	0.01351	0.01229	3.64×10^{-3}

σ_x, σ_y and σ_z are standard deviations and U is isotropic atomic displacement parameter. The U parameters for CO_2 (C12, O1, and O2) are those evaluated from anisotropic atomic displacement parameters ($U_{11} = 2.45 \times 10^{-3}$ nm^2, $U_{22} = 4.87 \times 10^{-3}$ nm^2, $U_{33} = 3.55 \times 10^{-3}$ nm^2, $U_{12} = 1.67 \times 10^{-3}$ nm^2, $U_{13} = 6.84 \times 10^{-5}$ nm^2, and $U_{23} = -1.50 \times 10^{-4}$ nm^2). The linear constraints for the atomic displacement parameters were imposed as follows: $U^{B} = U^{F} = U^{N} = U^{C(host)}$; $U^{Cu} = 0.25 \times U^{B}$; $U^{H} = 1.5 \times U^{B}$; and $U_{ij}^{C12} = U_{ij}^{O}$.

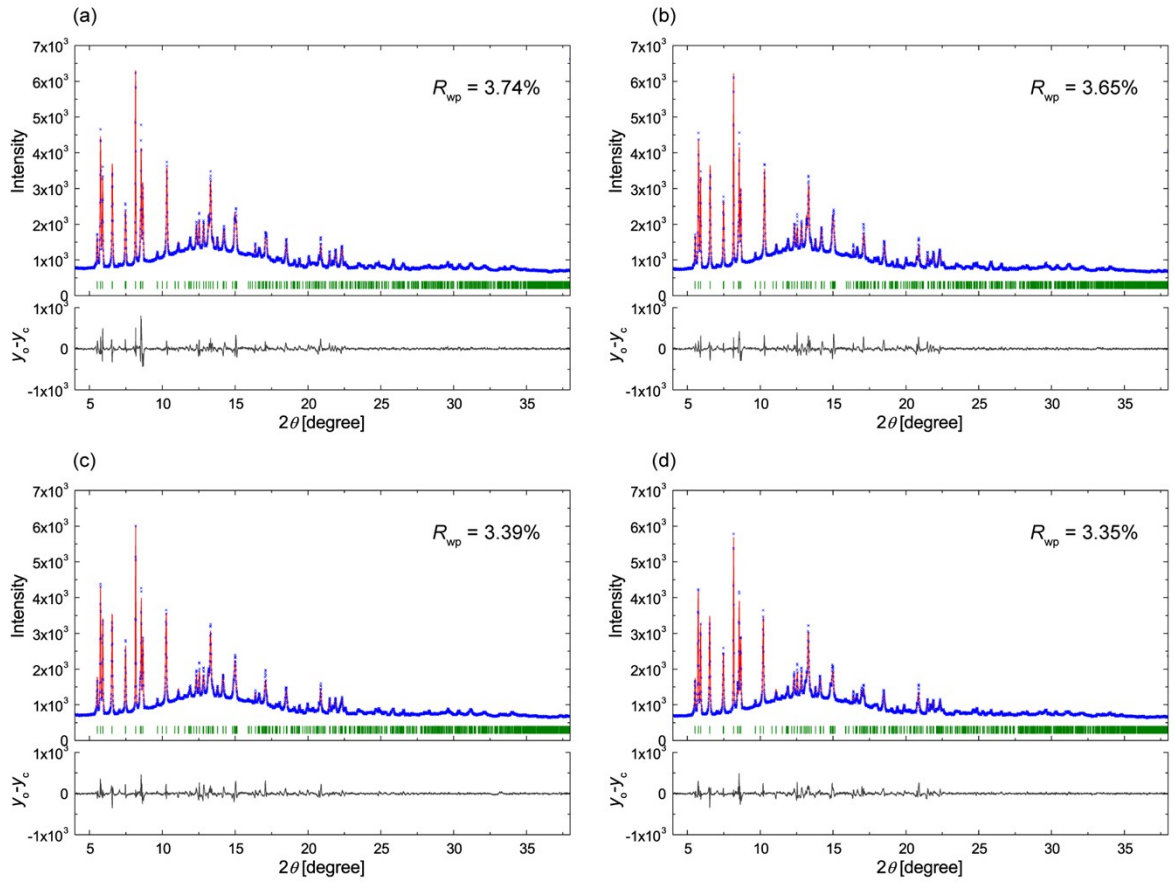

Fig. S4 Le Bail fitting pattern of ELM-11 at (a) 195 K, (b) 223 K, (c) 248 K, and (d) 298 K. The bottom panels show the residual error.

Table S6 Atomic coordinates of ELM-11 at 273 K in space group *C*2/*c*. Atom types of ELM-11 are shown in Fig. S3.

Atom	x	y	z	σ_x	σ_y	σ_z	U [nm^2]
Cu	0	0.19748	0.75	–	0.00097	–	7.95×10^{-5}
B	0.76309	0.11747	0.60732	0.00523	0.00471	0.00375	3.18×10^{-4}
F1	0.73463	0.05132	0.67095	0.00153	0.00212	0.00122	3.18×10^{-4}
F2	0.66401	0.17222	0.55809	0.00168	0.00189	0.00142	3.18×10^{-4}
F3	0.83849	0.20862	0.64247	0.00176	0.00190	0.00121	3.18×10^{-4}
F4	0.81184	0.04581	0.55625	0.00177	0.00220	0.00139	3.18×10^{-4}
N1	0.08925	0.21568	0.65847	0.00278	0.00334	0.00196	3.18×10^{-4}
N2	0	0.38048	0.75	–	0.00522	–	3.18×10^{-4}
N3	0	1.01519	0.75	–	0.00494	–	3.18×10^{-4}
C1	0.19109	0.25881	0.67978	0.00431	0.00356	0.00234	3.18×10^{-4}
C2	0.25652	0.27325	0.61711	0.00351	0.00341	0.00306	3.18×10^{-4}
C3	0.21637	0.24292	0.53312	0.00402	0.00436	0.00301	3.18×10^{-4}
C4	0.11672	0.20077	0.51267	0.00365	0.00444	0.00226	3.18×10^{-4}
C5	0.05014	0.18616	0.57563	0.00285	0.00417	0.00306	3.18×10^{-4}
C6	0.96691	0.44101	0.67579	0.00292	0.00309	0.00264	3.18×10^{-4}
C7	0.96615	0.56756	0.67412	0.00311	0.00308	0.00238	3.18×10^{-4}
C8	0	0.63160	0.75	–	0.00548	–	3.18×10^{-4}
C9	0	0.76434	0.75	–	0.00510	–	3.18×10^{-4}
C10	0.94313	0.82858	0.80394	0.00328	0.00316	0.00284	3.18×10^{-4}
C11	0.94445	0.95490	0.80269	0.00364	0.00311	0.00272	3.18×10^{-4}
H1	0.22311	0.28243	0.74447	–	–	–	4.77×10^{-4}
H2	0.33869	0.30816	0.63396	–	–	–	4.77×10^{-4}
H3	0.08439	0.17683	0.44809	–	–	–	4.77×10^{-4}
H4	0.96811	0.15139	0.55729	–	–	–	4.77×10^{-4}
H5	0.94129	0.39105	0.61827	–	–	–	4.77×10^{-4}
H6	0.93992	0.61433	0.61533	–	–	–	4.77×10^{-4}
H7	0.90127	1.00494	0.84364	–	–	–	4.77×10^{-4}
H8	0.89895	0.78188	0.84584	–	–	–	4.77×10^{-4}

σ_x, σ_y and σ_z are standard deviations and U is isotropic atomic displacement parameter. The linear constraints for the atomic displacement parameter were imposed as follows: $U^{B} = U^{F} = U^{N} = U^{C}$; $U^{Cu} = 0.25 \times U^{B}$; and $U^{H} = 1.5 \times U^{B}$.

Table S7 Atomic charges from the Mulliken population analysis. Atom types are shown in Fig. S3.

Temperature	195 K	223 K	248 K	273 K	298 K
Atom	q [e]	q [e]	q [e]	q [e]	q [e]
Cu	0.642	0.615	0.619	0.615	0.621
B	0.799	0.791	0.786	0.774	0.788
F1	–0.426	–0.392	–0.386	–0.408	–0.390
F2	–0.346	–0.379	–0.361	–0.368	–0.365
F3	–0.435	–0.421	–0.423	–0.421	–0.426
F4	–0.420	–0.416	–0.434	–0.399	–0.433
N1	–0.403	–0.401	–0.403	–0.382	–0.400
N2	–0.443	–0.454	–0.457	–0.465	–0.446
N3	–0.423	–0.410	–0.419	–0.409	–0.412
C1	0.077	0.089	0.087	0.088	0.087
C2	–0.121	–0.132	–0.128	–0.120	–0.136
C3	0.114	0.029	0.034	0.046	0.061
C4	–0.131	–0.086	–0.093	–0.046	–0.112
C5	0.069	0.087	0.084	0.052	0.071
C6	0.117	0.103	0.109	0.106	0.104
C7	–0.055	–0.058	–0.054	–0.073	–0.058
C8	0.038	0.052	0.042	0.077	0.048
C9	–0.033	0.009	–0.006	0.038	–0.011
C10	–0.098	–0.103	–0.093	–0.118	–0.100
C11	0.114	0.096	0.104	0.098	0.101
H1	0.165	0.167	0.162	0.147	0.161
H2	0.182	0.168	0.168	0.181	0.185
H3	0.120	0.123	0.121	0.161	0.121
H4	0.145	0.160	0.157	0.128	0.159
H5	0.147	0.155	0.157	0.169	0.159
H6	0.159	0.186	0.184	0.122	0.185
H7	0.183	0.169	0.172	0.154	0.178
H8	0.145	0.160	0.160	0.183	0.158

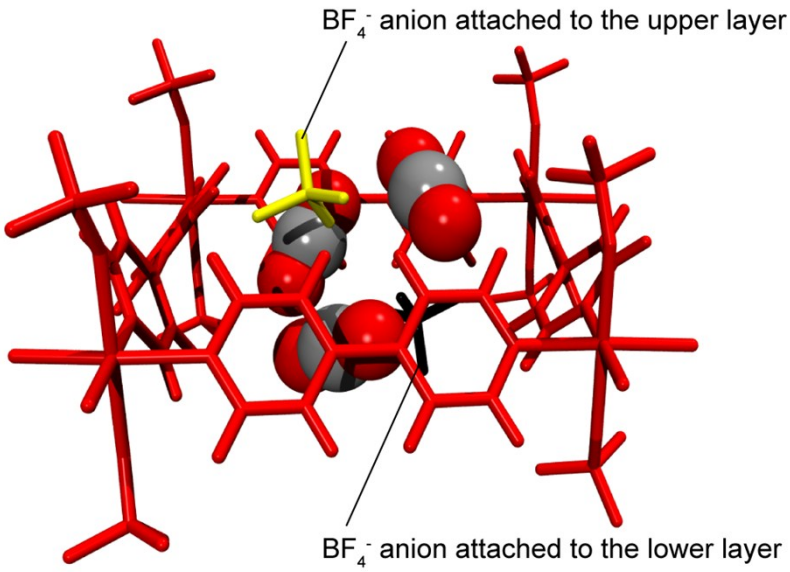

Fig. S5 Snapshot of three CO_2 molecules encapsulated in a square grid. The configuration was obtained by GCMC simulation at 52 kPa and 195 K.

Table S8 Comparison of bond lengths before and after the geometry optimization by DFT-D3 method. Atom types are shown in Fig. S3.

	ELM-11		ELM-11 ⊃ $2CO_2$	
Bond length [nm]	before optimization	after optimization	before optimization	after optimization
Cu-F3	0.240	0.264	0.219	0.259
B-F3	0.143	0.144	0.145	0.145
B-F1	0.137	0.142	0.142	0.142
B-F2	0.136	0.142	0.140	0.143
B-F4	0.147	0.141	0.140	0.139
Cu-N2	0.204	0.204	0.207	0.202
N2-C6	0.137	0.135	0.141	0.135
C6-C7	0.141	0.139	0.140	0.139
C7-C8	0.141	0.140	0.140	0.140
C8-C9	0.148	0.148	0.141	0.148
C9-C10	0.141	0.140	0.138	0.140
C10-C11	0.141	0.139	0.139	0.139
C11-N3	0.137	0.135	0.136	0.135
Cu-N1	0.201	0.201	0.208	0.201
N1-C5	0.138	0.135	0.133	0.135
C5-C4	0.143	0.139	0.142	0.139
C4-C3	0.131	0.141	0.136	0.141
C3-C3	0.148	0.148	0.150	0.148
C3-C2	0.140	0.140	0.135	0.140
C2-C1	0.142	0.138	0.139	0.138
C1-N1	0.134	0.135	0.134	0.135
Cu-N3	0.204	0.206	0.202	0.200

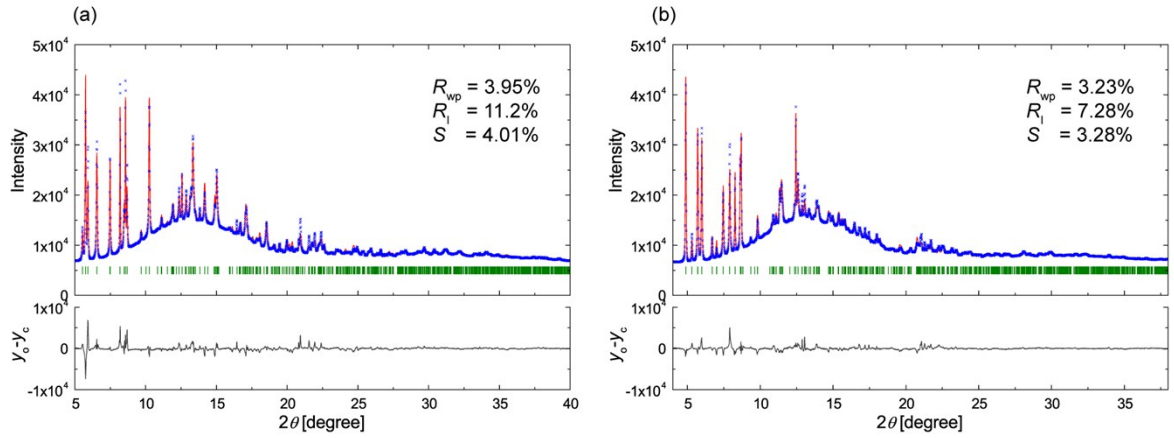

Fig. S6 Rietveld refinement XRPD patterns using the optimized structures obtained by DFT-D3 method as initial models: (a) ELM-11 at 273 K, and (b) ELM-11 ⊃ $2CO_2$ at 273 K. Only the parameters of the profile function and atomic displacement parameters were refined.

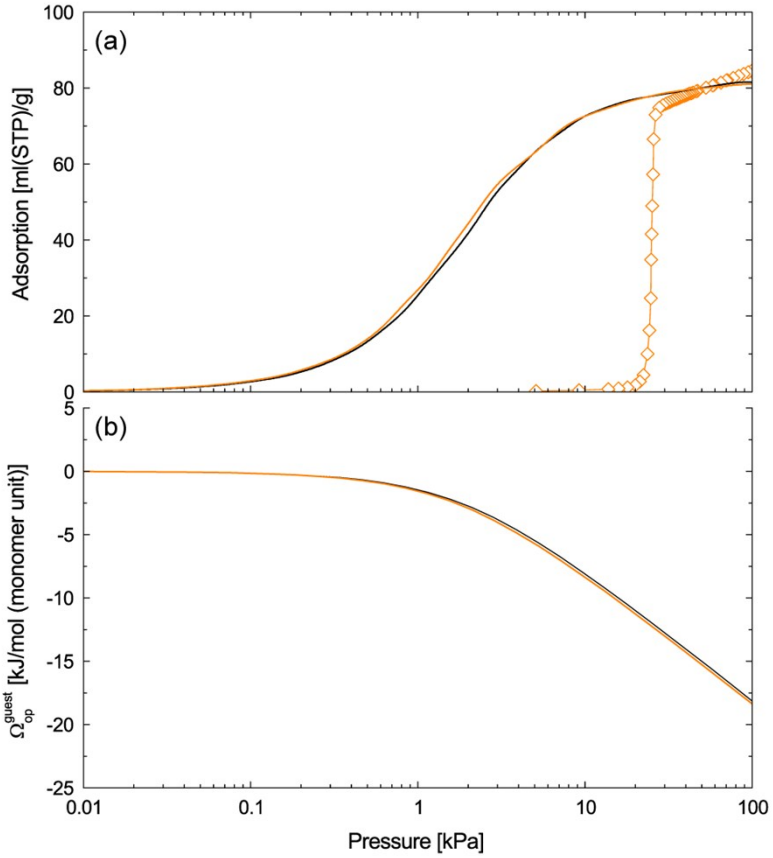

Fig. S7 (a) Fictitious adsorption isotherms obtained by the GCMC simulations using the structures before (orange) and after (black) the geometry optimization by DFT-D3 method together with the experimental desorption isotherm of CO_2 on ELM-11 at 273 K. (b) The grand potentials of guest obtained by integrating the fictitious adsorption isotherms.

§2 Structure refinement method based on hybrid reverse Monte Carlo simulation

In this section, we demonstrate the structure refinement method based on hybrid reverse Monte Carlo (MC) simulation, using which the initial structure of closed ELM-11 was determined. In this method, the acceptance probability for an MC trial move, P_{acc}, is given by

$$P_{acc} = \min\left\{1, \exp\left(\frac{R_{wp,new} - R_{wp,old}}{S} + w\frac{U_{new} - U_{old}}{k_B T}\right)\right\}, \quad \text{(S1)}$$

where $R_{wp,new}$ and $R_{wp,old}$ are the reliability factors of the new and old configuration; S is a scaling factor; w is a weighting factor; U_{new} and U_{old} are the total interaction potentials of the new and old configuration; k_B is the Boltzmann constant; and T is temperature. The reliability factor R_{wp}, which represents the goodness of fit between the observed and calculated XRPD diagrams, is represented as

$$R_{wp} = 100 \times \sqrt{\frac{\sum_i w_i (y_i - y_{c,i})^2}{\sum_i w_i y_i}}, \quad \text{(S2)}$$

where y_i is the ith intensity of the experimental powder diffraction pattern; $y_{c,i}$ is the calculated intensity from the structure model; and w_i is a weighting factor ($w_i = 1/y_i$ is used conventionally).

Trial Moves. Several trial moves based on the symmetry of the space group ($C2/c$) were performed in the MC simulation. The symmetry axes and points in the ELM-11 structure (1 × 1 × 1 unit cell) are shown in Fig. S8. The employed MC moves are as follows: (i) rotation of bpy I about the centre of symmetry located between the pyridine rings; (ii) translation of the centre of mass of bpy II along the twofold axis (C_2), rotation of bpy II about the C_2 axis and bond rotation (C–C–C–C torsion) between the pyridine rings of bpy II; (iii) translation of the centre of mass of BF_4 and rotation of BF_4; and (iv) translation of a Cu atom. The pyridine ring, BF_4, and CO_2 were treated as rigid bodies during the simulation.

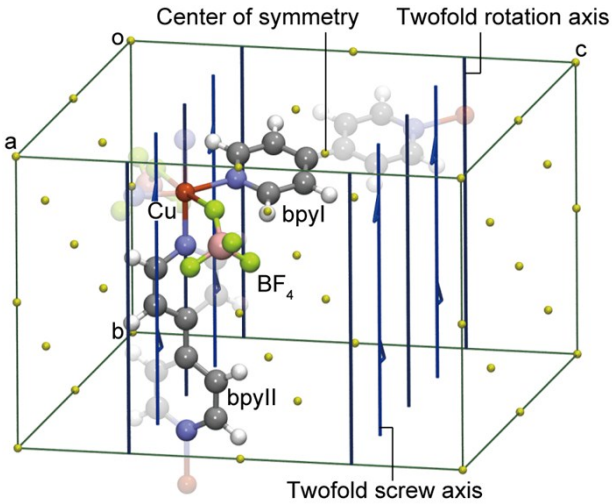

Fig. S8 Part of the simulation cell of closed ELM-11 for Monte Carlo simulation (1 × 1 × 1 unit cell). The translucent atoms are those produced by symmetry operations.

Interaction Potentials. The total interaction potentials of ELM-11, U, can be divided into a bonded term and a non-bonded term:

$$U = U_{bonded} + U_{nonbonded} = U_{bonded} + U_{Coulombic} + U_{LJ} \quad \text{(S3)}$$

Two bond stretching terms (Cu–N and Cu–F), two angle bending terms (N–Cu–N and N–Cu–F), and one bond rotation term between the pyridine rings of bpy (C–C–C–C) were considered as components of the bonded potential, and all the remaining degrees of freedom were rigidly constrained. The bond potential functions of each component were adopted from our previous work.[2] The non-bonded term (sum of the Coulombic and LJ potentials) was calculated in the same manner as discussed in the experimental section, except that the LJ size parameter of hydrogen, σ_H, was set to be zero to take into account the formation of a hydrogen bond.

Reliability Factors. The R_{wp} factor of the new configuration after an MC step was evaluated using the RIETAN-

2000[3] software package. The split pseudo-Voigt function was used to describe the peak profile of the calculated XRPD pattern, and only the parameters of the profile function were refined before the evaluation of the R_{wp} factor.

Parameter Settings. The S factor works in a manner analogous to the way temperature works in the conventional MC simulations. We determined $S = 0.03$ by trial and error so that the R_{wp} factor decreases smoothly. The weighting factor of $w = 0.036$ was used so that the contributions of the energy term and the R_{wp} term were nearly equal. Temperature was set to 273 K.

We first constructed an initial configuration of closed ELM-11 with the unit cell parameters, which were obtained from the Le Bail fitting to the observed XRPD pattern at 273 K, by deforming and arranging the open framework structure of ELM-11. The initial structure was then relaxed for 2×10^4 MC steps by setting $w = 0$, after which another 3×10^4 MC steps were performed by setting $w = 0.036$. Fig. S9 shows changes in the total potential energy and the R_{wp} factor of the closed ELM-11 structure during the hybrid reverse MC simulation, which demonstrates that the closed structure of ELM-11 was successfully converged to that having both a low potential energy and a small R_{wp} value.

We finally chose the closed ELM-11 structure with the smallest ($R_{wp}/S + wU/T$) value, which is the exponent of the acceptance probability, as an initial structure model of closed ELM-11 for the Rietveld refinement, as mentioned in the experimental section.

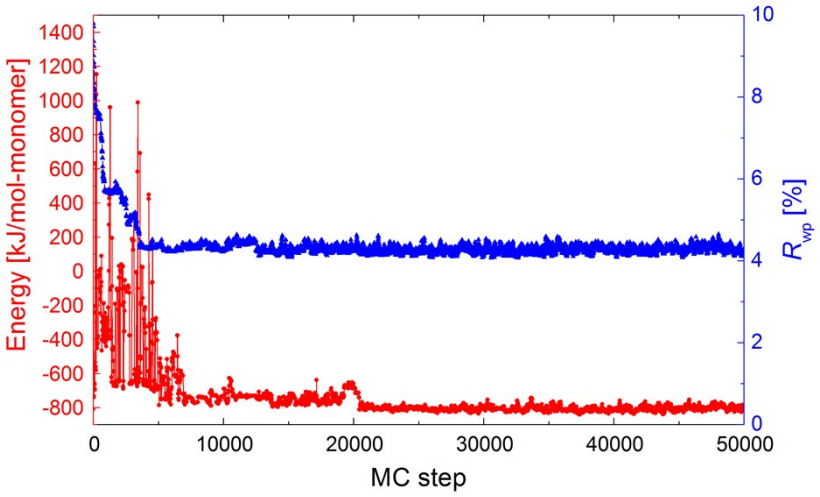

Fig. S9 Total potential energy and the R_{wp} factor of the closed ELM-11 structure during the hybrid reverse MC simulation.

Reference

1. Y. F. Chen, J. Y. Lee, R. Babarao, J. Li and J. W. Jiang, *J. Phys. Chem. C*, 2010, **114**, 6602–6609.
2. H. Tanaka, S. Hiraide, A. Kondo and M. T. Miyahara, *J. Phys. Chem. C*, 2015, **119**, 11533–11543.
3. F. Izumi and T. Ikeda, *Mater. Sci. Forum*, 2000, **321–324**, 198–203.