Supporting Information for

Universal Gas-Uptake Behavior of a Zeolitic Imidazolate Framework ZIF-8 at High Pressure

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PART I. Supplementary Figures

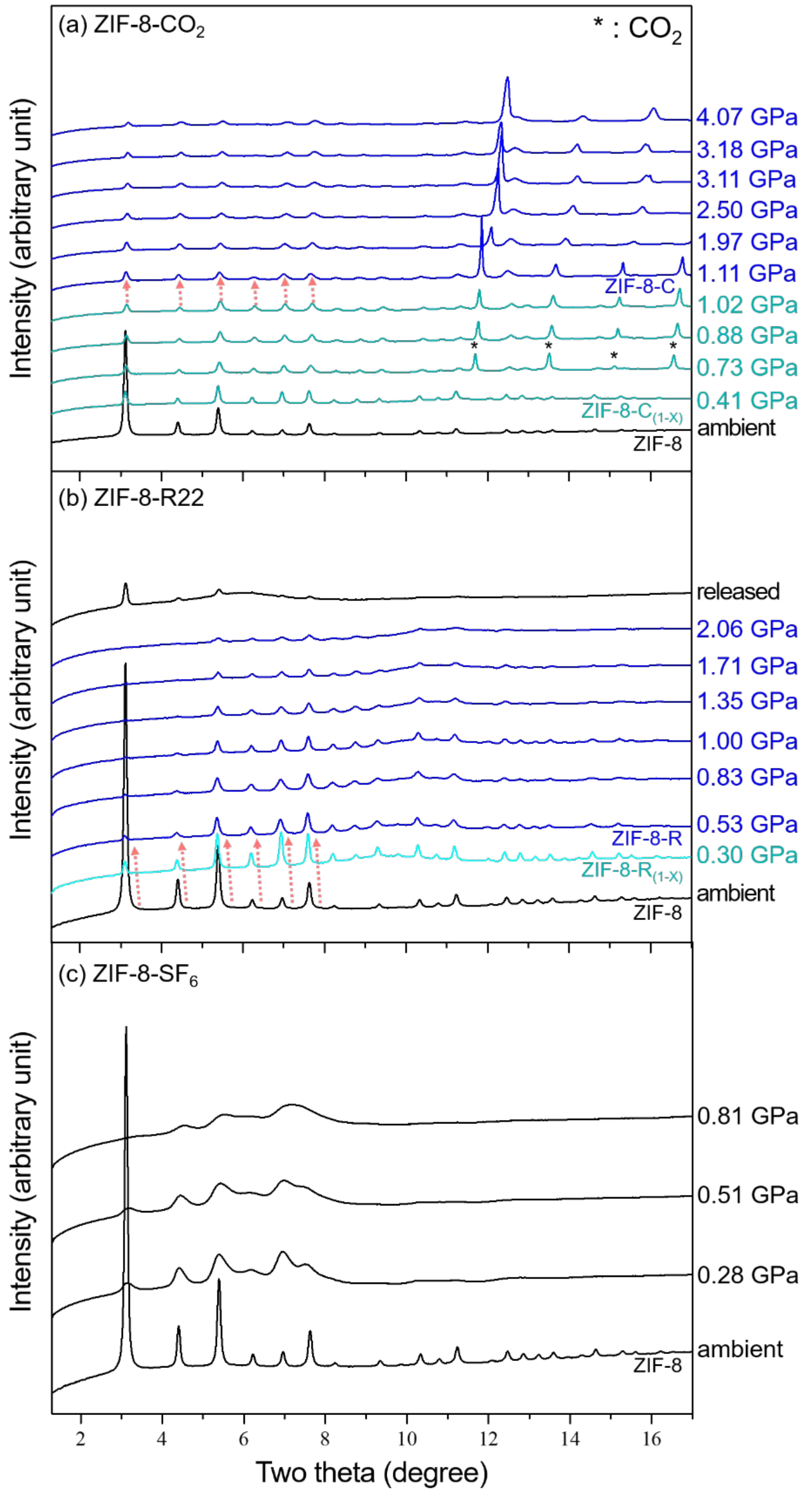


Figure S1. Diffraction patterns of ZIF-8 at high pressures. ZIF-8-PII denotes a state where pressure-induced insertion (PII) of the different gases (C: CO_2, R: R22, S: SF_6) is saturated, whereas the subscript (1-x) denotes a stage where PII is in progress. Note ZIF-8 compressed with SF_6 shows peak broadening at relatively low pressures compared to those compressed with CO_2 and R22.

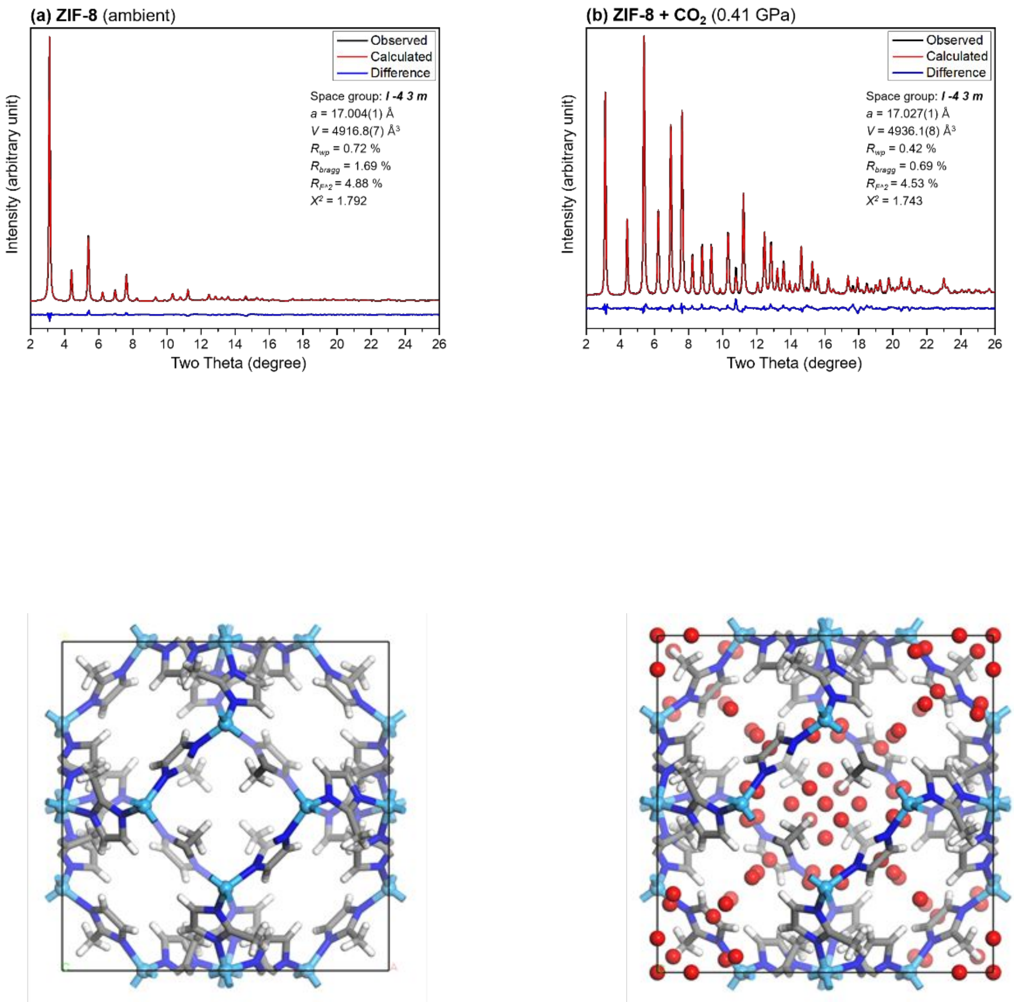
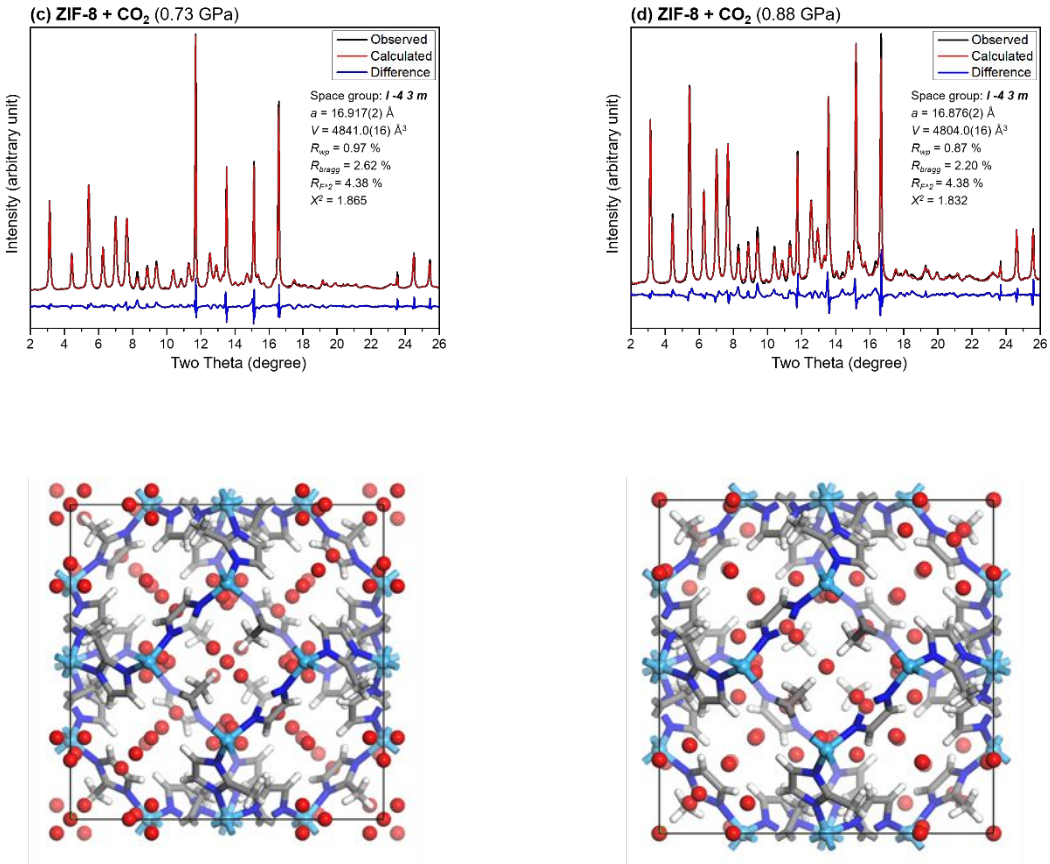


Figure S2. Rietveld fits of ZIF-8 at different pressures in CO_2 pressure medium with respective structural models using oxygen dummy atoms. (a) ambient, (b) 4.1 kbar, (c) 7.3 kbar, (d) 8.8 kbar, (e) 10.2 kbar, (f) 11.1 kbar, (g) 19.7 kbar, (h) 25.0 kbar, (i) 31.1 kbar, (j) 31.8 kbar, (k) 40.7 kbar.

Figure S2. (continued)



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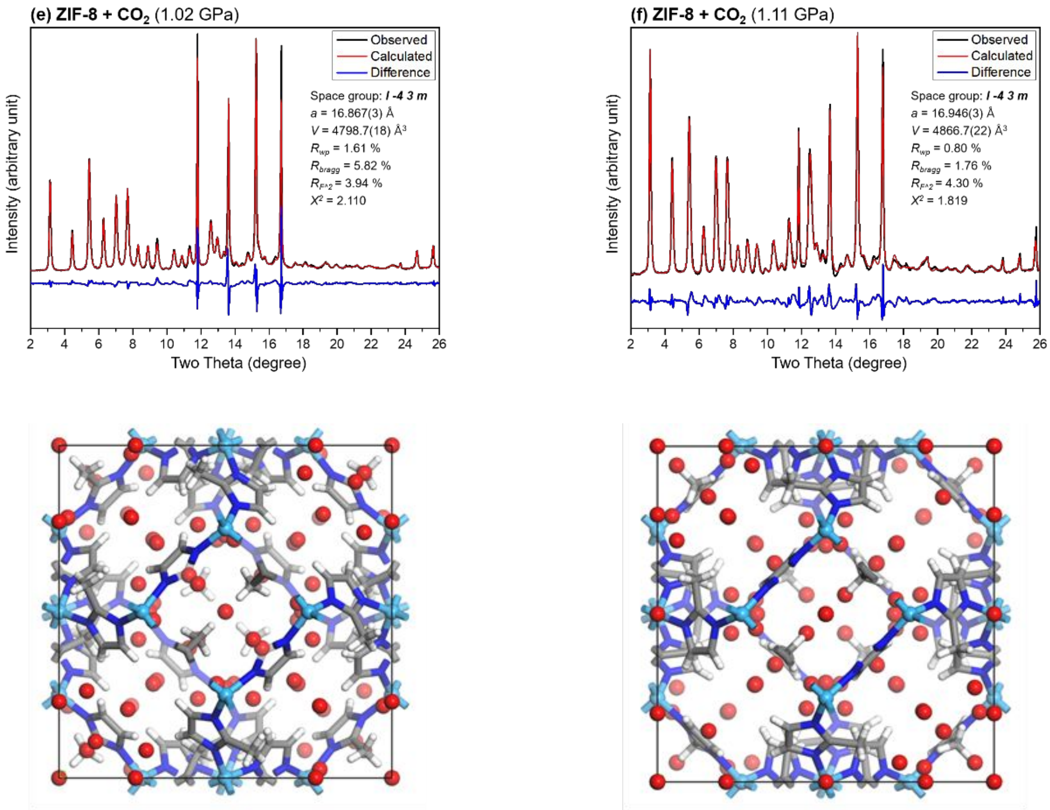

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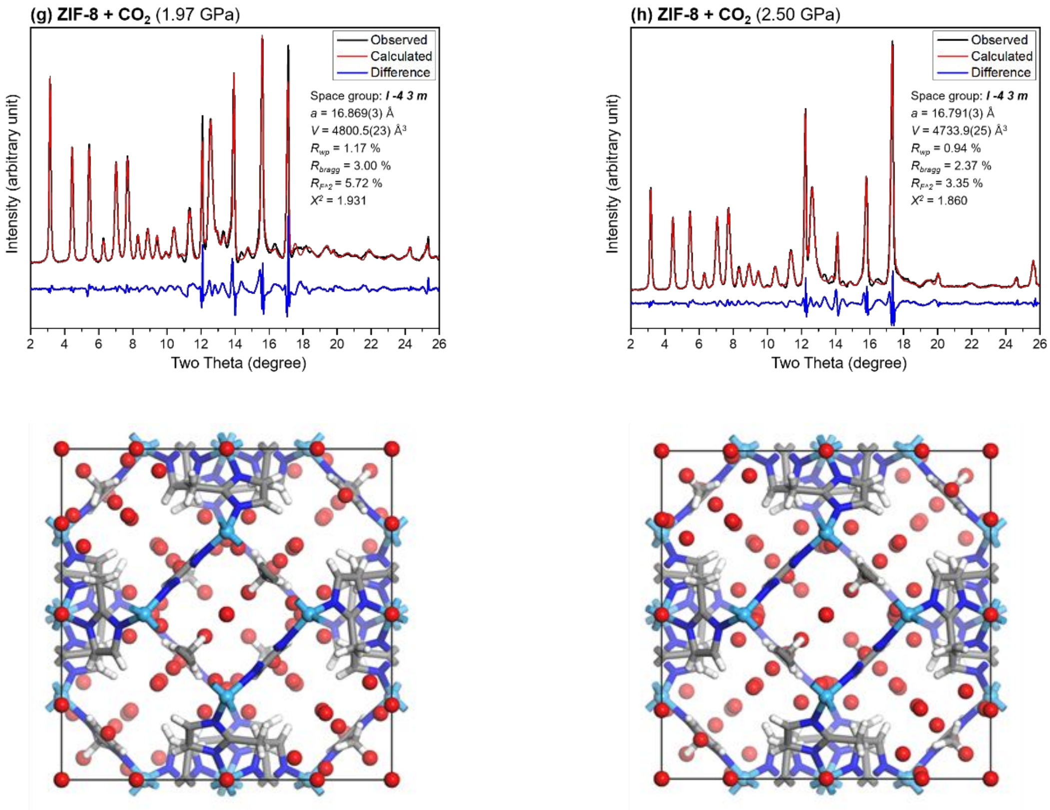

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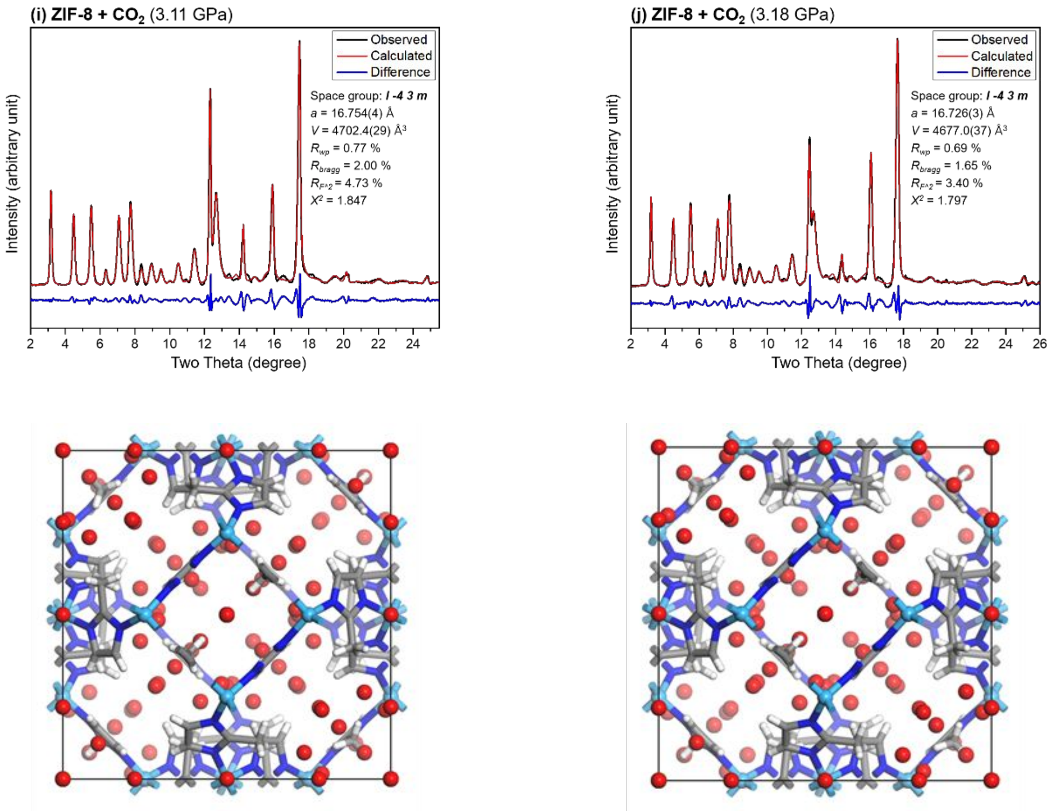

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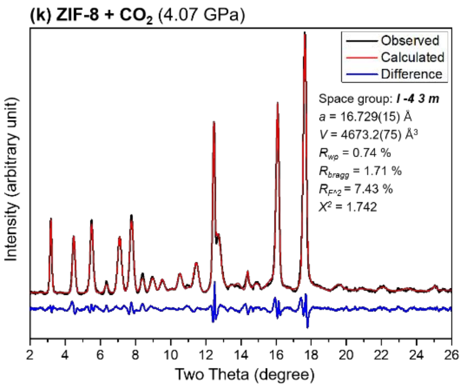
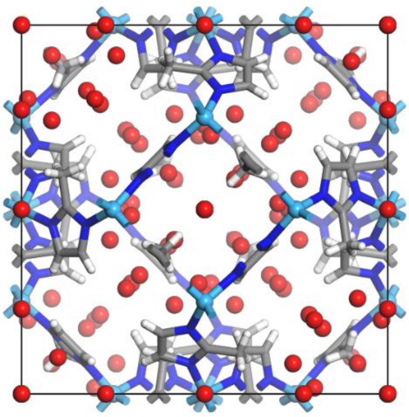




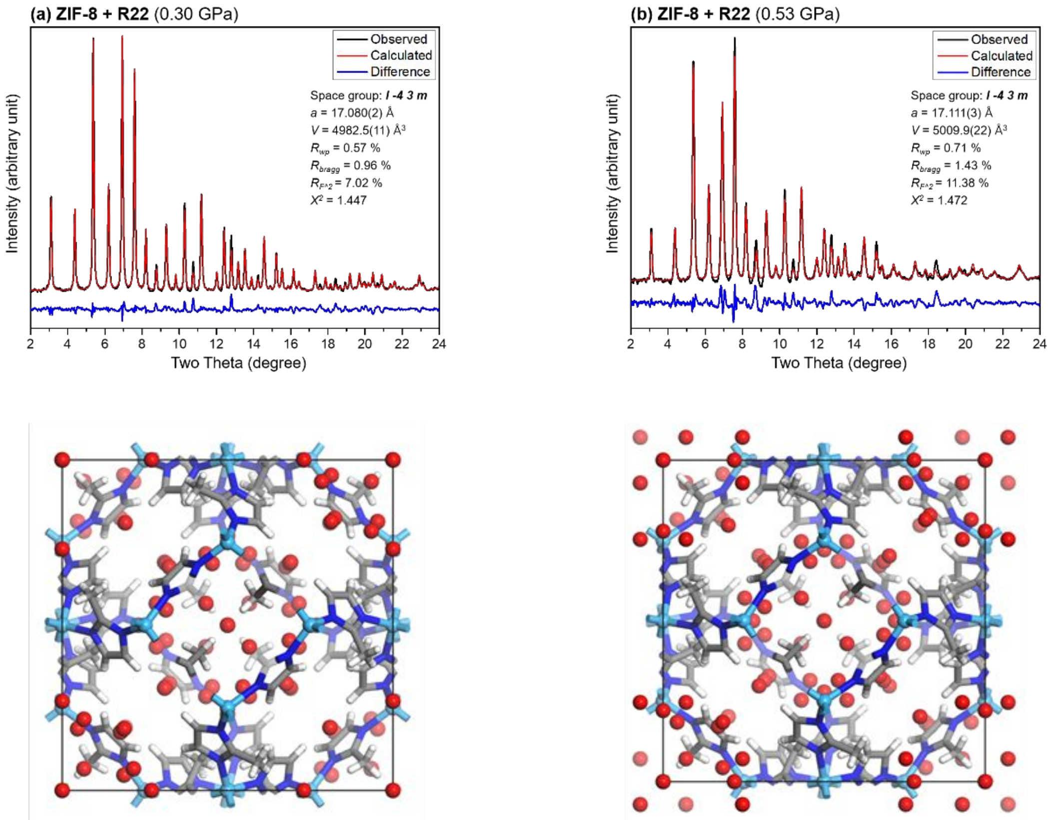
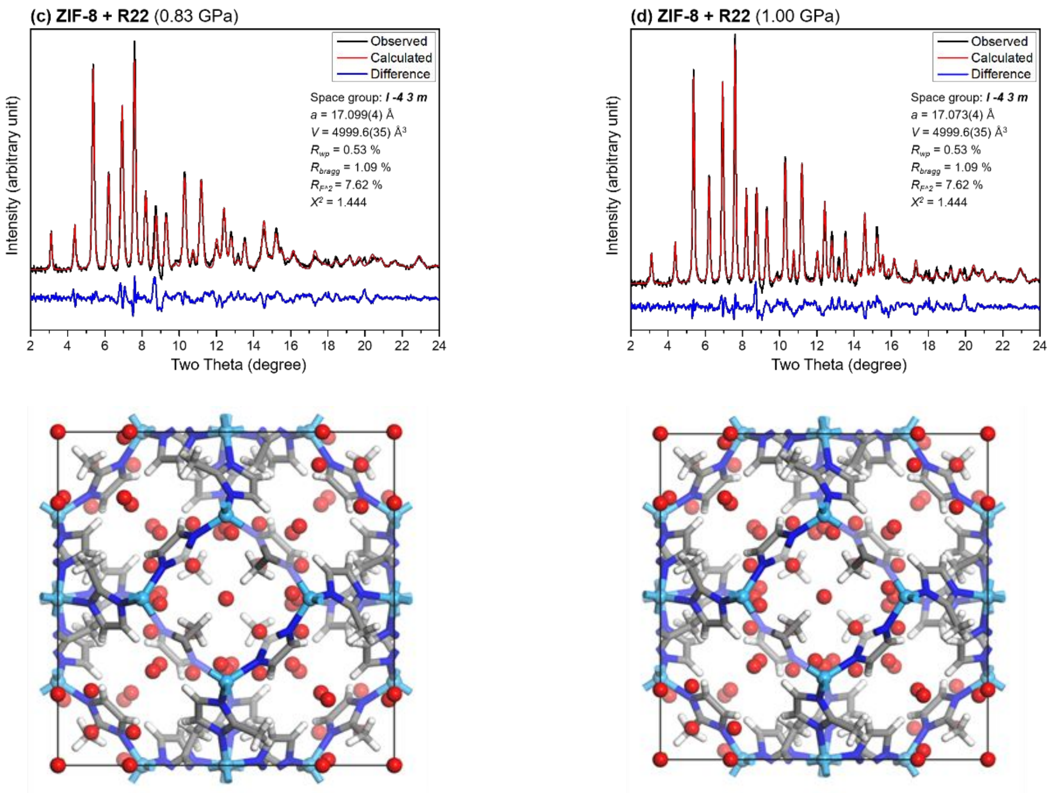


Figure S3. Rietveld fits of ZIF-8 at different pressures in R22 pressure medium with respective structural models using oxygen dummy atoms. (a) 3.0 kbar, (b) 5.3 kbar, (c) 8.3 kbar, (d) 10.0 kbar, (e) 13.5 kbar, (f) 17.1 kbar, (g) 20.6 kbar.

Figure S3. (continued)



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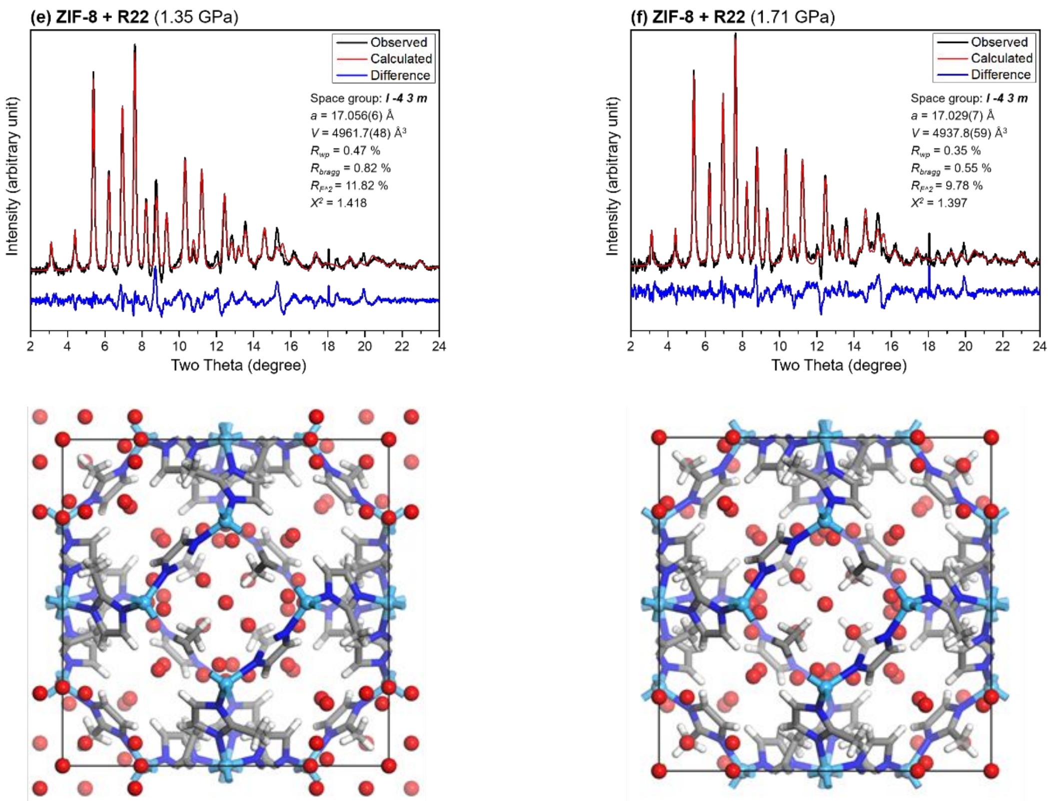

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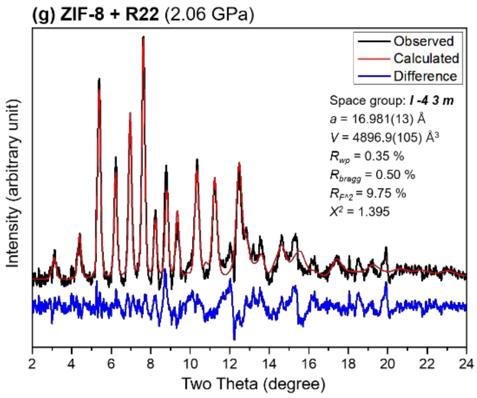

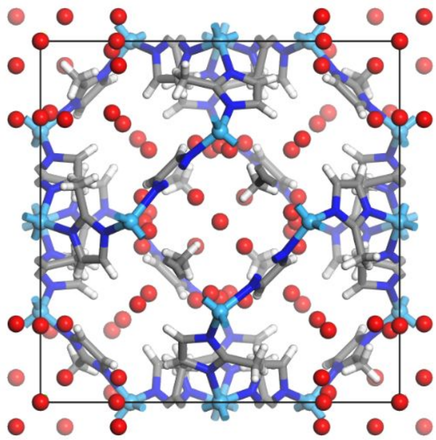

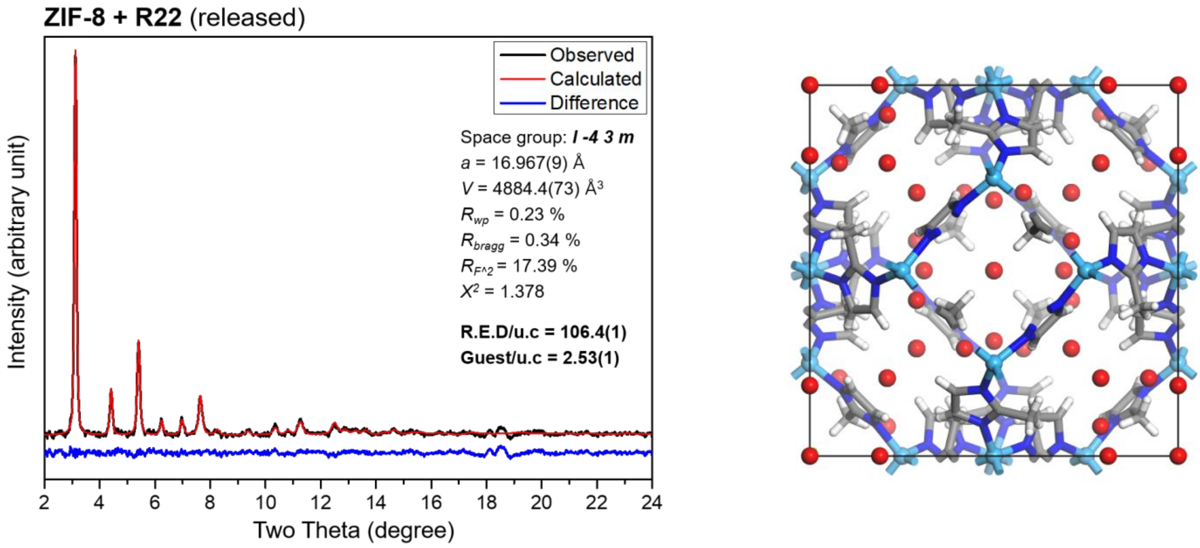

Figure S4. A Rietveld fit and structure model of pressure-released ZIF-8 after compression in the presence of R22. Based on the residual electron density, the number of R22 molecules contained per unit cell is estimated to 2.53(1).

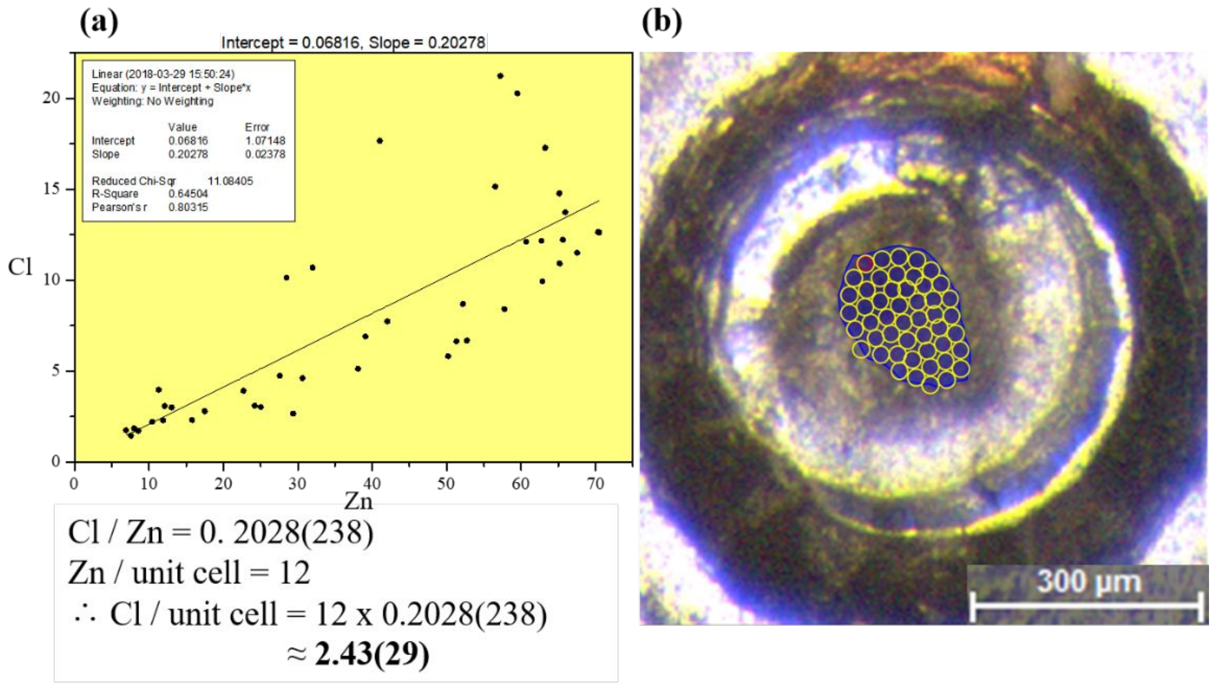

Figure S5. X-ray fluorescence spectroscopy of ZIF-8 after pressure release in the presence of R22. The number of residual R22 molecules are obtained from linear-fitting of the measured Cl/Zn counts. Total 49 points were scanned over the recovered ZIF-8 sample in the gasket hole, and 41 points that were not disturbed by stainless-steel gasket surrounding the sample were used for analysis. The Cl to Zn ratio at each point was linearly fitted to give 2.4(1) R22 molecules per unit cell, which agrees with the Rietveld result (Fig. S4). (a) The result of the linear fit of Cl/Zn counts. (b) An image of the recovered sample with yellow circles indicating XRF probed regions.

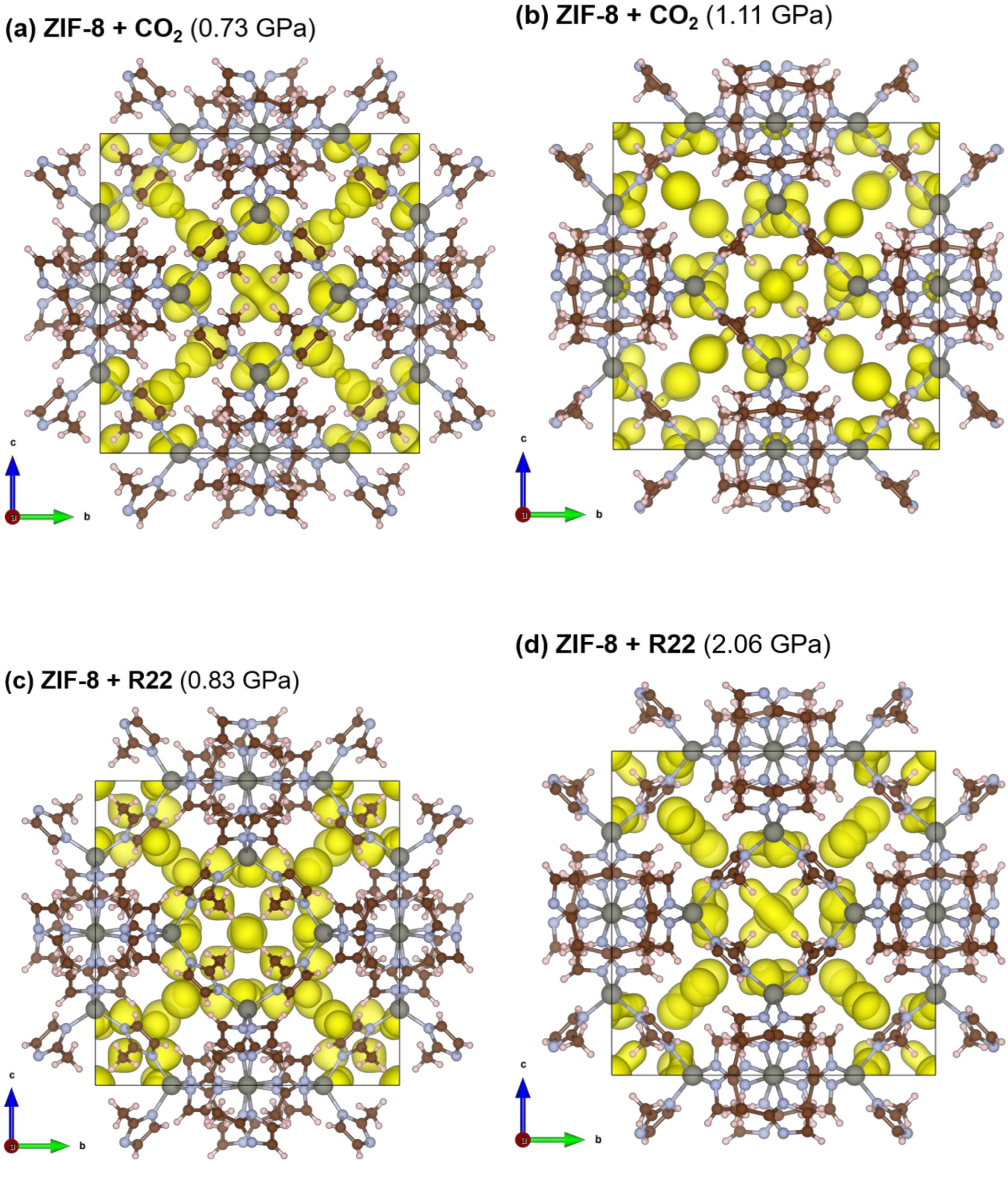

Figure S6. Electron density maps calculated from Rietveld refinement. Changes in ZIF-8 framework is accompanied by changes in electron density distribution with increasing pressure. The unit cells are viewed along [100] direction. Note the incomplete pore opening of ZIF-8 compressed up to 20.6 kbar with R22, compared to ZIF-8 at 11.1 kbar in CO_2 PTM.

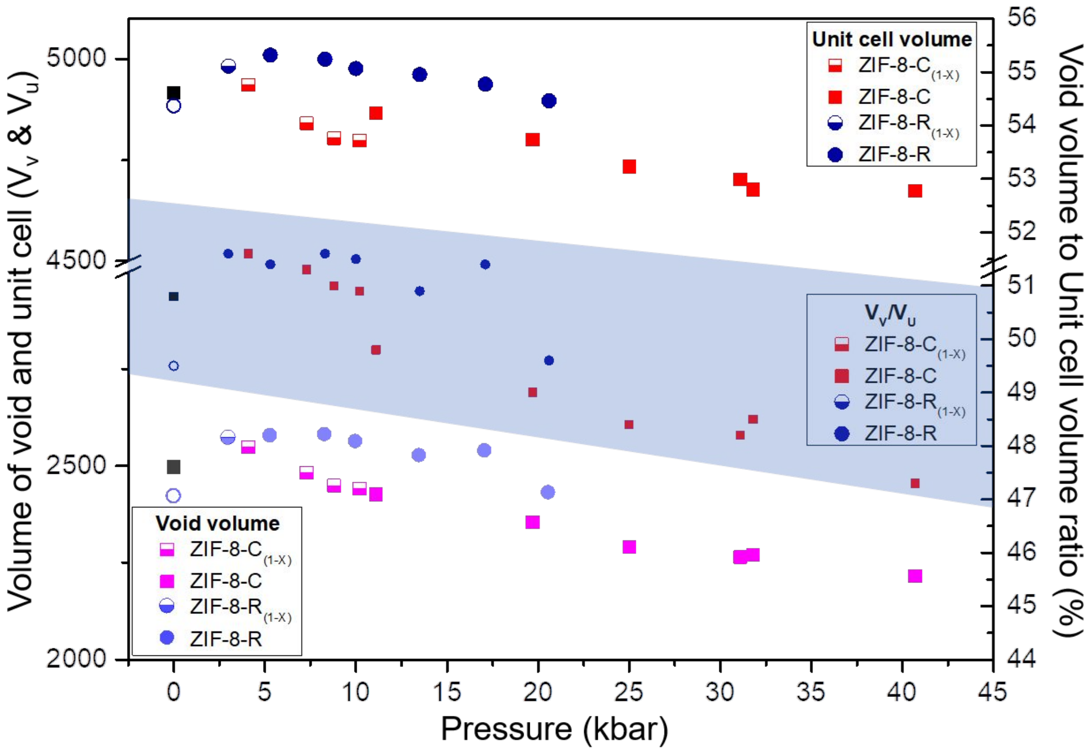

Figure S7. Unit cell and void volumes of ZIF-8 as a function of pressure. The data points within the blue-shaded envelope show the ratio of void and unit cell volumes in percent. Note that the void to unit cell volume ratio decreases with increasing pressure.

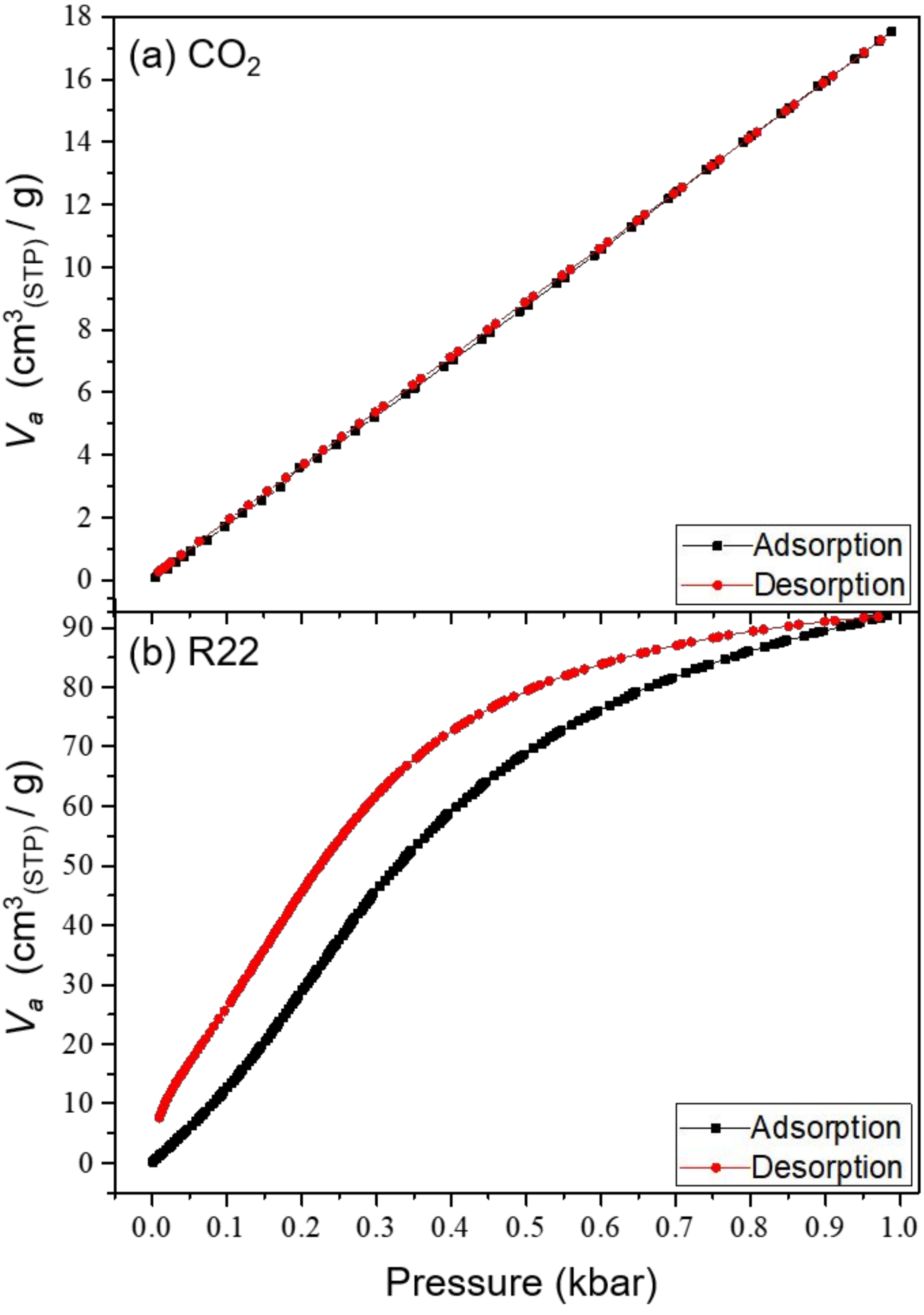

Figure S8. Adsorption/desorption isotherms of ZIF-8 under (a) CO_2 and (b) R22 atmospheres. The amount adsorbed is estimated by the gas volume at standard conditions (V_a). Note that R22 shows a higher degree of hysteresis and a certain amount of remnant gas after desorption, indicating its higher interaction with the framework compared to CO_2.

PART II. Supplementary Tables

Table S1. Framework and pore data for ZIF-8 under CO_2 PTM

Pressure [kbar]	Unit cell Volume (V_U) [Å^3]	Void Volume (V_V) [Å^3] [a]	V_V/V_U [%]	Torsion angle [^{0}][b]	Electron Count[c]	CO_2 molecules
0	4917(1)	2539	50.8	60.0	0	0
4.1	4936(1)	2571	51.6	58.9	882	40.1
7.3	4841(2)	2500	51.3	60.2	1003	45.6
8.8	4804(2)	2445	51.0	60.2	1042	47.4
10.2	4799(2)	2468	50.9	60.3	1072	48.7
11.1	4867(3)	2524	49.8	84.4	1167	53.0
19.7	4801(3)	2498	49.0	85.1	1230	55.9
25.0	4734(3)	2410	48.4	86.8	1231	56.0
31.1	4702(3)	2388	48.2	86.5	1232	56.0
31.8	4677(4)	2356	48.5	85.5	1233	56.1
40.7	4673(8)	2350	47.3	83.2	1234	56.1

[a] Calculated using *Mercury CSD 3.10.3* with a probe radius of 1.2 Å. [b] The angle between mean plane of imidazolate and crystallographic (100) plane.
[c] Obtained from Rietveld refinement.

Table S2. Framework and pore data for ZIF-8 under R22 PTM

Pressure [kbar]	Unit cell Volume (V_U) [Å^3]	Void Volume (V_V) [Å^3] [a]	V_V/V_U [%]	Torsion angle [^{0}][b]	Electron Count[c]	R22 molecules
0	4917(1)	2539	50.8	66.0	0	0
3.0	4983(2)	2571	51.6	61.2	926	22.0
5.3	5010(3)	2576	51.4	62.3	1053	25.1
8.3	5000(4)	2579	51.6	61.6	1068	25.4
10.0	4977(3)	2561	51.5	59.8	1070	25.5
13.5	4962(5)	2524	50.9	67.1	1084	25.8
17.1	4938(6)	2537	51.4	61.0	1083	25.8
20.6	4897(11)	2428	49.6	76.1	1084	25.8
0 (released)	4884(8)	2419	49.5	75.8	106	2.53

[a] Calculated using *Mercury CSD 3.10.3* with a probe radius of 1.2 Å. [b] The angle between mean plane of imidazolate and crystallographic (100) plane.
[c] Obtained from Rietveld refinement.