Supporting Information for

High-Pressure Chemistry of a Zeolitic Imidazolate Framework Compound in the Presence of Different Fluids

Junhyuck Im[1], Narae Yim[2], Jaheon Kim[2], Thomas Vogt,[3] and Yongjae Lee[1,4,*]

[1]Department of Earth System Sciences, Yonsei University, Seoul 03722, Korea.

[2]Department of Chemistry, Soongsil University, Seoul 06978, Korea.

[3]NanoCenter and Department of Chemistry & Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States

[4]Center for High Pressure Science & Technology Advanced Research (HPSTAR), Shanghai 201203, China.

Corresponding Author

*Email: yongjaelee@yonsei.ac.kr, Tel.:+82-2-2123-5667.

PART I. Experimental Details

Synthesis of ZIF-8. Zinc nitrate tetrahydrate ($Zn(NO_3)_2 \cdot 6H_2O$; 0.146 g, 0.49 mmol) was dissolved in 10 mL methanol. Separately, 2-methylimidazole (0.325 g, 3.96 mmol) was also dissolved in 10 mL methanol. The zinc salt solution was poured quickly into the ligand solution, and the resulting mixture was slowly stirred for 2 hours at room temperature. The white precipitates were collected by centrifuging the product mixture. The collected solid was washed with neat methanol (3 × 25 mL) and dried at 50 °C in a convection oven for 24 hours.[1]

Synchrotron X-ray diffraction. *In situ* synchrotron X-ray powder diffraction experiments were performed at the beamline 10-2 at the Stanford Synchrotron Radiation Lightsource (SSRL) and the beamline 5A at the Pohang Accelerator Laboratory (PAL). At the SSRL, a focused X-ray beam with a wavelength of 0.6199(1) Å was used. The XRD patterns of ZIF-8 in the presence of different PTM (Table s1) were obtained using a Pilatus 300K-w direct photon counting detector. The detector exhibits gaps near 8.2 and 12.8 degrees as indicated in Figure 2a, 2b and 2d. At beamline 5A at the PAL, monochromatic hard X-ray photons emitted from an in-vacuum undulator source were monochromatized to a wavelength of 0.6926(1) Å and were detected using a MAR-345 imaging plate detector. The wavelength of the incident beam and the detector calibrations were carried out using LaB_6 standard reference material (SRM 660b) at both synchrotron facilities.

High-pressure experiments. A modified Merrill-Bassett type diamond anvil cell (DAC) with two opposed diamonds supported by tungsten-carbide plates[2] was used for the high-pressure XRD measurements. The anvils used were brilliant-cut type-1A diamonds with a culet diameter of 700 μm. The DAC has a rectangular asymmetric slot on one side to provide an opening of ca. 40 degrees, through which diffraction data are measured. The powdered sample was loaded into a 350 μm diameter and less than 150 μm thick sample chamber obtained by electro-spark erosion in a pre-indented stainless steel foil gasket. A few ruby spheres of ~10 μm diameter were added as a pressure gauge. Subsequently, a powdered sample of as-synthesized ZIF-8 was added to the sample chamber and either water, methanol,

ethanol or silicone oil was added as a hydrostatic pressure transmitting media (PTM). The pressure at the sample in the DAC was measured by detecting the shift of R1 emission line of included ruby spheres (precision: ± 0.05 GPa).[3] The pressure was calculated using the equation below (1):

$$P = A / B [1 + (\Delta\lambda / \lambda_0)]^B \quad (1)$$

where P is the pressure in megabars, λ is the wavelength of the ruby R line, A = 19.04 Mbar, B = 7.665.[4] The sample was equilibrated for about 10 minutes in the DAC at each measured pressure. Changes in the unit cell lengths and volume were derived from a series of whole profile fitting procedure using the GSAS suite of programs.[5-6]

Part II. Supporting Figure

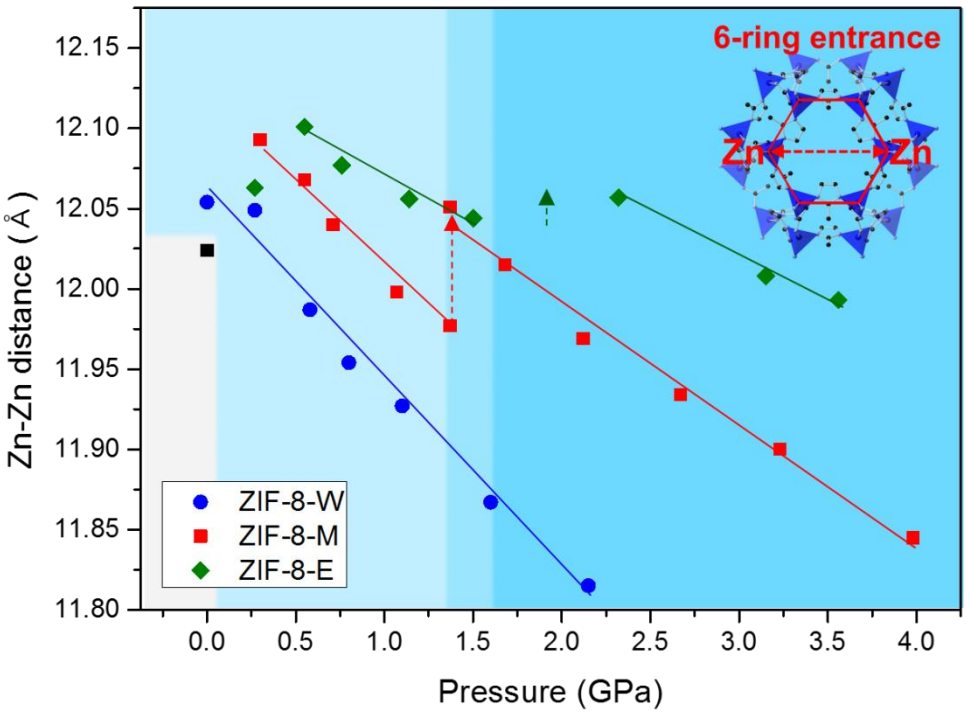

Figure S1. Pressure-dependent changes of Zn-Zn distance in the 6-ring entrance of the ZIF-8 framework in the presence of water (W), methanol (M), and ethanol (E) pressure transmitting medium conditions.

Part III. Supporting Tables

Table S1. Summary of the pressure-dependent behavior of ZIF-8 with various pressure transmitting media (PTM).

PTM	P_t (GPa)[a]	β (GPa^{-1})[b]	K_0 (GPa)[c]	Synchrotron Facilities
water		0.03143	41.71	BL10-2 at SSRL
methanol	1.4	0.02703	40(2)	BL10-2 at SSRL
ethanol	2.3	0.01754	73(4)	BL5A at PAL
silicone oil			20(5)	BL10-2 at SSRL

[a] P_t: pressure of the phase transition

[b] β: compressibility of ZIF-8-$PII_{(1-x)}$ phases

[c] K_0: bulk moduli (BM) of ZIF-8 (silicone oil PTM) and ZIF-8-PII phases (K_0': fixed at 4)

Table S2. Changes of the unit cell parameters, volumes, residual electron density and inserted guest molecules as a function of pressure in ZIF-8.[a]

PTM	P (GPa)	treatment	phase	space group	a (Å)	V (Å^3)	Residual electron density	Guest molecules
	0	ambient	ZIF-8	**I-***43m*	17.031(2)	4940(2)	0	0
	0	wet	ZIF-8-W$_{(1-x)}$	**I-***43m*	17.047(1)	4954(1)	198(26)	20(3)
	0.27		ZIF-8-W$_{(1-x)}$	**I-***43m*	17.039(2)	4948(2)	481(33)	48(3)
	0.58		ZIF-8-W$_{(1-x)}$	**I-***43m*	16.951(1)	4871(1)	520(29)	52(3)
W (H_2O)	0.8		ZIF-8-W$_{(1-x)}$	**I-***43m*	16.905(2)	4832(1)	523(29)	52(3)
	1.1		ZIF-8-W$_{(1-x)}$	**I-***43m*	16.866(1)	4798(1)	556(26)	56(3)
	1.6		ZIF-8-W	**I-***43m*	16.782(4)	4727(3)	619(66)	62(7)
	2.16		ZIF-8-W	**I-***43m*	16.709(4)	4665(4)	708(26)	71(3)
	0	released	ZIF-8	**I-***43m*	16.927(4)	4850(3)		
	0	ambient	ZIF-8	**I-***43m*	17.004(2)	4916(2)	0	0
	0.3		ZIF-8-M$_{(1-x)}$	**I-***43m*	17.1015(6)	5001.6(5)	352(18)	20(1)
	0.55		ZIF-8-M$_{(1-x)}$	**I-***43m*	17.0658(7)	4970.3(6)	484(17)	26.9(9)
	0.71		ZIF-8-M$_{(1-x)}$	**I-***43m*	17.0269(8)	4936.4(7)	521(19)	29(1)
	1.07		ZIF-8-M$_{(1-x)}$	**I-***43m*	16.9680(9)	4885.3(7)	584(16)	32.5(9)
	1.37		ZIF-8-M$_{(1-x)}$	**I-***43m*	16.954(1)	4873.4(9)	635(27)	35(2)
MeOH			ZIF-8-M	**I-***43m*	17.059(1)	4964.0(9)		
(CH_3OH)	1.68		ZIF-8-M$_{(1-x)}$	**I-***43m*	16.912(1)	4837(1)		
			ZIF-8-M	**I-***43m*	16.9801(6)	4895.7(6)	654(22)	36(1)
	2.12		ZIF-8-M	**I-***43m*	16.9273(5)	4850.2(5)	648(19)	36(1)
	2.67		ZIF-8-M	**I-***43m*	16.8779(6)	4807.9(5)	674(23)	37(1)
	3.23		ZIF-8-M	**I-***43m*	16.8292(5)	4766.4(4)	669(16)	37.2(9)
	3.98		ZIF-8-M	**I-***43m*	16.7506(5)	4699.9(4)	686(18)	38(1)
	0	released	ZIF-8	**I-***43m*	16.954(2)	4873(2)		
	0	ambient	ZIF-8	**I-***43m*	17.014(1)	4925(1)	0	0
	0.3		ZIF-8-E$_{(1-x)}$	**I-***43m*	17.0592(6)	4964.5(6)	288(27)	11(1)
	0.6		ZIF-8-E$_{(1-x)}$	**I-***43m*	17.111(1)	5010(1)	460(33)	18(1)
	0.8		ZIF-8-E$_{(1-x)}$	**I-***43m*	17.078(1)	4980.5(9)	478(26)	18(1)
	1.1		ZIF-8-E$_{(1-x)}$	**I-***43m*	17.047(1)	4954.0(9)	482(30)	19(1)
EtOH	1.5		ZIF-8-E$_{(1-x)}$	**I-***43m*	17.031(1)	4939.7(9)	520(21)	20(1)
(C_2H_5OH)	2.3		ZIF-8-E	**I-***43m*	17.050(2)	4957(1)	573(21)	22(1)
	3.2		ZIF-8-E	**I-***43m*	16.981(2)	4896(2)	662(26)	25(1)
	3.6		ZIF-8-E	**I-***43m*	16.9619(8)	4880.0(7)	661(42)	25(2)
	0	released	ZIF-8	**I-***43m*	16.9707(4)	4887.6(4)		

	0	ambient	ZIF-8	**I-***43m*	17.031(2)	4940(2)
Silicone Oil	0.3		ZIF-8-O	**I-***43m*	17.013(1)	4925(1)
	0.5		ZIF-8-O	**I-***43m*	16.892(4)	4820(4)

[a] ESD's are in parentheses.

Part IV. References

(1) Cravillon, J.; Münzer, S.; Lohmeier, S.-J.; Feldhoff, A.; Huber, K.; Wiebcke, M. *Chem. Mater*. **2009**, *21*, 1400.

(2) Mao, H. O. K.; Hemley, R. J. *Philos. Trans. A Math. Phys. Eng. Sci.* **1996,** *354*, 1315.

(3) Bell, P. M.; Mao, H. K. *Absolute pressure measurements and their comparison with the ruby fluorescence (R1) pressure scale to 1.5 Mbar*; Carnegie Institution: Carnegie Institution of Washington Year Book, 1979; pp 665-669.

(4) Mao, H. K.; Xu, J.; Bell, P. M. *J. Geophys. Res.-Solid* **1986,** *91*, 4673.

(5) Larson, A. C.; Dreele, R. B. V. *GSAS-General Structure Analysis System*; Los Alamos National Laboratory: 1986.

(6) Toby, B. H. *J. Appl. Crystallogr.* **2001,** *34*, 210.