<Supporting Information>

Topologies of Metal-Organic Frameworks Based on Pyrimidine-5-carboxylate and Unexpected Gas Sorption Selectivity for CO_2

Jinwoo Seo, Narae Jin and Hyungphil Chun*

Department of Applied Chemistry, College of Science and Technology, Hanyang University
1271, Sa-3 dong, Ansan 426-791, Republic of Korea.

List of contents

Page

Note on the crystal structures of **3** and **3**·Toluene. ····· S2

Table S1. Summary of crystal data for **3** and **3**·Toluene. ····· S3

Figure S1-2. TGA plots of **2** and **3**. ····· S4

Figure S3. FR-IR spectra of **3**. ····· S5

Figure S4-5. Interpenetration and overlaid structures of **3**. ····· S6

Figure S6. ORTEP plots of **3**·DMF, **3**, **3**·Toluene. ····· S7

Figure S7-8. X-ray structures of **3**·DMF and **3**·Toluene. ····· S8

Figure S9-10. Ar and CH_4 sorption isotherms. ····· S9

Figure S11-12. H_2 and N_2 sorption isotherms. ····· S10

Figure S13. O_2 sorption isotherms. ····· S11

*Note on the crystal structure refinements for **3** and **3**·Toluene:* For **3**, after anisotropic refinements of all the non-hydrogen atoms followed by the addition of hydrogen atoms, the diffused electron densities resulting from the residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON. The results of SQUEEZE process were attached to the cif file. For **3**·Toluene, the asymmetric unit is four times that of **3**·DMF (or **3**), and therefore the unit cell contains 12 solvent channels (3 in **3**·DMF). Toluene molecules are found ordered only in two-thirds of all the solvent channels, and the remaining channels show highly disordered electron densities nearby the framework atoms. The diffused electron densities in one-third of the solvent channels could not be modeled or removed by the SQUEEZE process, and therefore left without further treatment. This results in the poor GOF and R-factors as shown in Table S1; however, the disorder is strictly localized to the solvent regions and the framework is not affected at all. We also note that the solvent exchange with toluene causes the as-synthesized crystals crack down to smaller pieces, and thus a highly intense X-ray beam from synchrotron sources was necessary for the successful structure determination. The crystallographic asymmetric units of **3**·DMF, **3** and **3**·Toluene are shown in Fig S6.

Table S1. Summary of crystal data and structure refinements.

	3	**3**·Toluene
Formula	$Cu(C_5H_3N_2O_2)_2$	$[Cu(C_5H_3N_2O_2)_2]\cdot 1/6(C_7H_8)$
FW	309.73	325.08
T (K)	173(2)	100(2)
λ (Å)	0.71073	0.72000
Crystal system	Rhombohedral	Rhombohedral
Space group	*R*-3	*R*-3
Unit cell dimensions	a = 21.593(3) Å	a = 43.571(6) Å
	c = 7.740(1) Å	c = 7.718(2) Å
V (Å^3)	3125.4(7)	12689(4)
Z	9	36
ρ_{calcd} (g/cm^3)	1.481	1.532
μ (mm^{-1})	1.586	1.566
F(000)	1395	5880
Crystal size (mm^3)	0.50 × 0.20 × 0.20	0.24 × 0.08 × 0.06
Reflections collected	6284	32276
Independent reflections (R_{int})	1676 (0.0179)	6537 (0.1102)
T_{max} / T_{min}	0.7421 / 0.5044	0.9119 / 0.7049
Data/restraints/parameters	1676 / 0 / 88	6537 / 84 / 407
GOF on F^2	1.333	1.863
R_1, wR_2 [$I > 2\sigma(I)$]	0.0571, 0.1173	0.1459, 0.4305
R_1, wR_2 (all data)	0.0634, 0.1188	0.1700, 0.4600
Extinction coefficient	–	0.012(1)
Largest different peak/hole (e/Å^3)	0.468 / -1.755	4.440 / -1.812

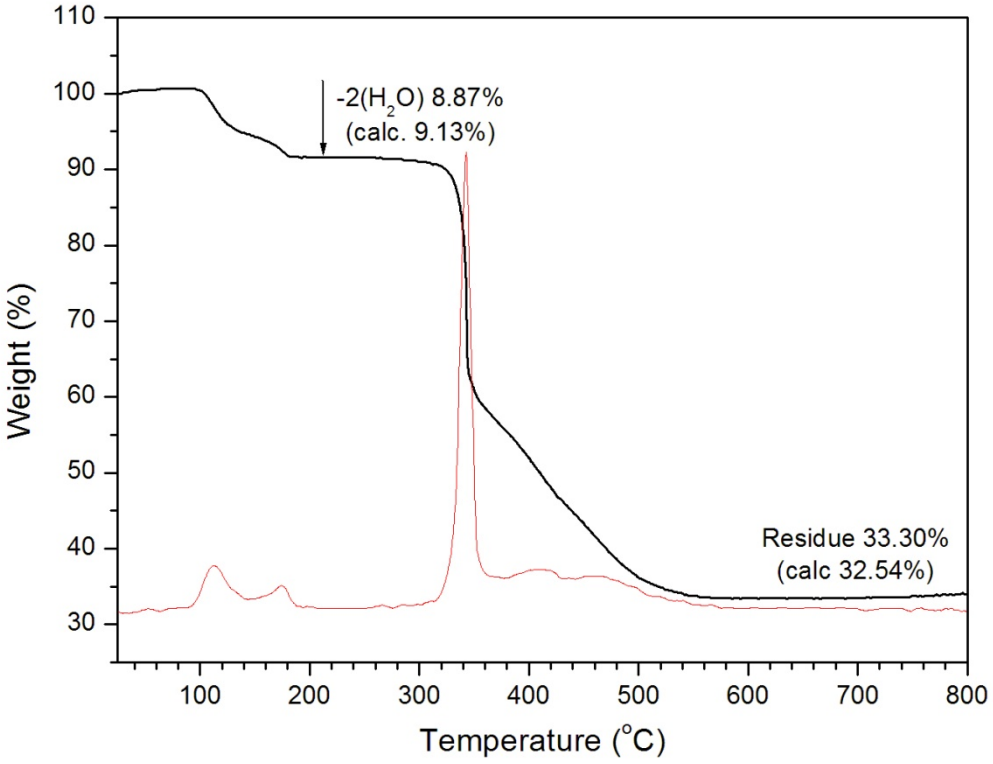

Figure S1. TGA plot of as-synthesized **2**. The red line is the first derivative.

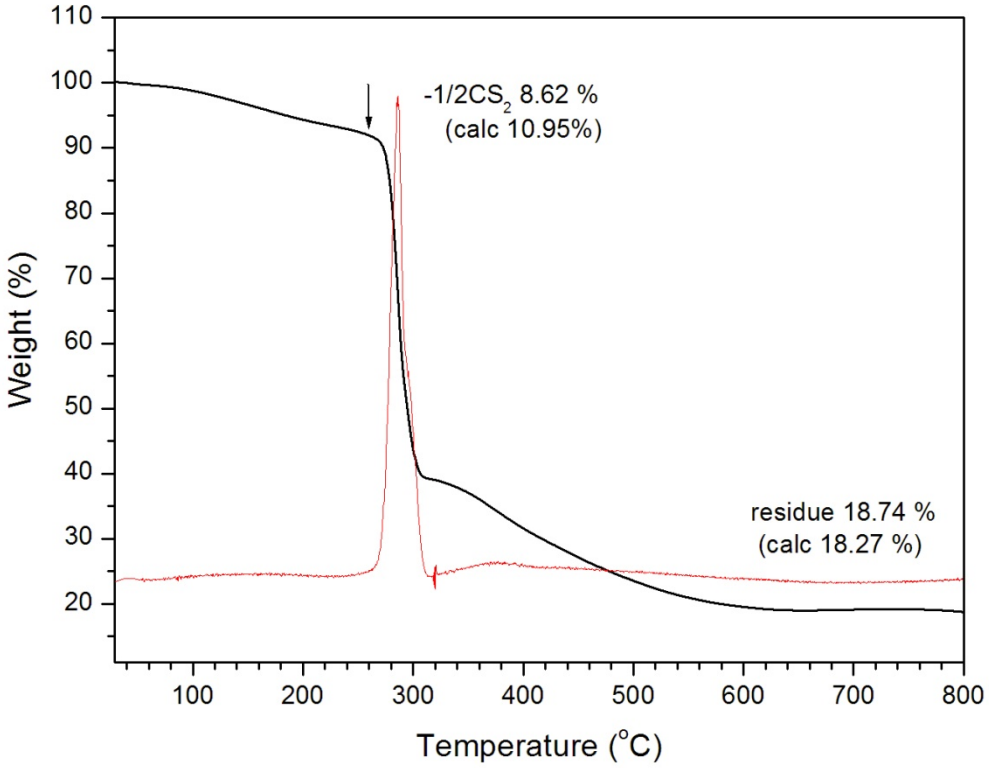

Figure S2. TGA plot of **3** after guest-exchange with CS_2. The red line is the first derivative.

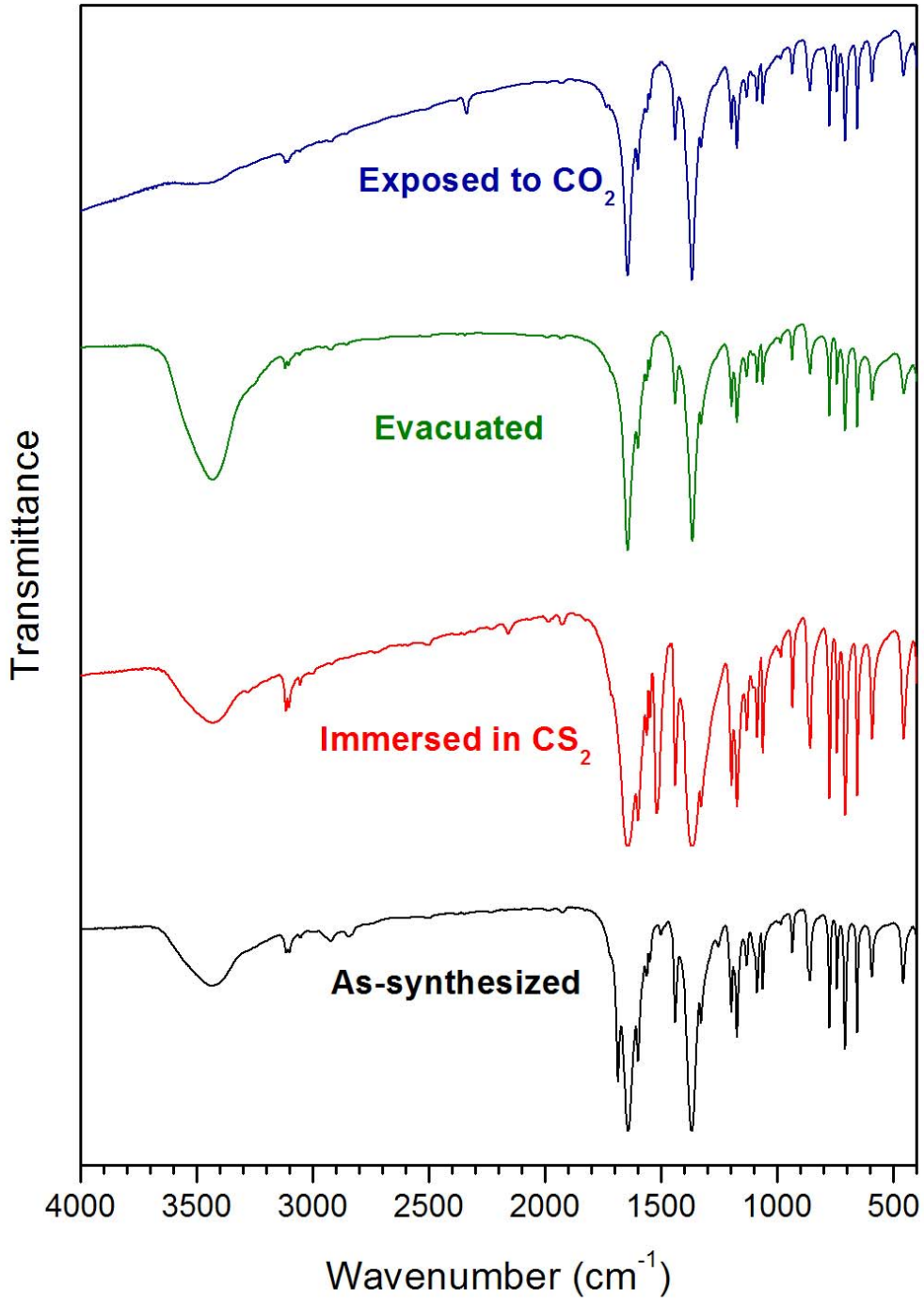

Figure S3. FT-IR spectra of $Cu(pmc)_2$ (**3**) measured as KBr pellets under various conditions.

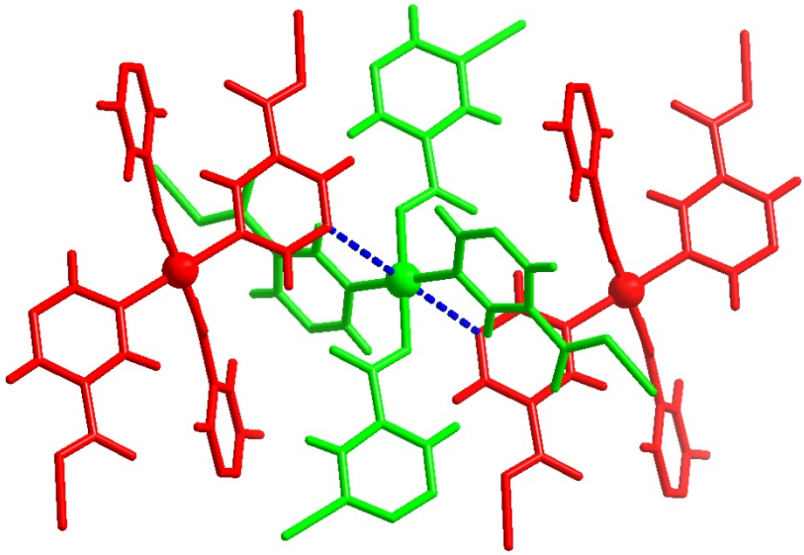

Figure S4. The weak N· · ·Cu· · ·N interactions (broken line) between two interpenetrating nets of **3**. A search in the Cambridge Structure Database (v. 5.31) reveals that there are many similar examples in which square planar Cu^{2+} in N_2O_2 coordination environment forms intermolecular contact of 3.2 – 3.3 Å. CSD Refcode: AJIKOT, BAMXET, BEMRER, BEWKEU, BIDQUA01, CACRAZ10, CUJCUF, DOBFIJ, FEPJAL, FEVTEG, GOLSAC, HIHBUV, HIHBUV01, IBODIM, IQIQAA, IYETEL, JANPET, JODFEO, JODGEP, KOJNAZ, LULXIZ, MEJNEV, MEMDUD, OFONUT, PAHYAZ01, PUHKUY, QAQMIF, QILFIA, QIRYOF, SAJJUJ, SUGMIQ, UDAJUF, UJUMIV, VERQEP, VIJRUB, VOMLIS, WATWET, WIHBOE, ZZZTWE02.

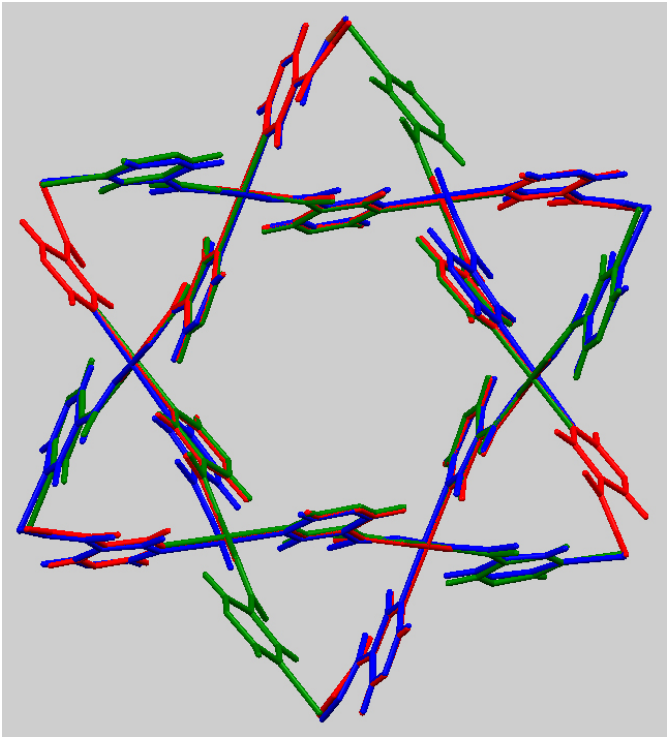

Figure S5. X-ray crystal structures of **3**·DMF (green), **3** (red) and **3**·toluene (blue) overlaid by fitting the positions of 6 Cu^{2+} ions.

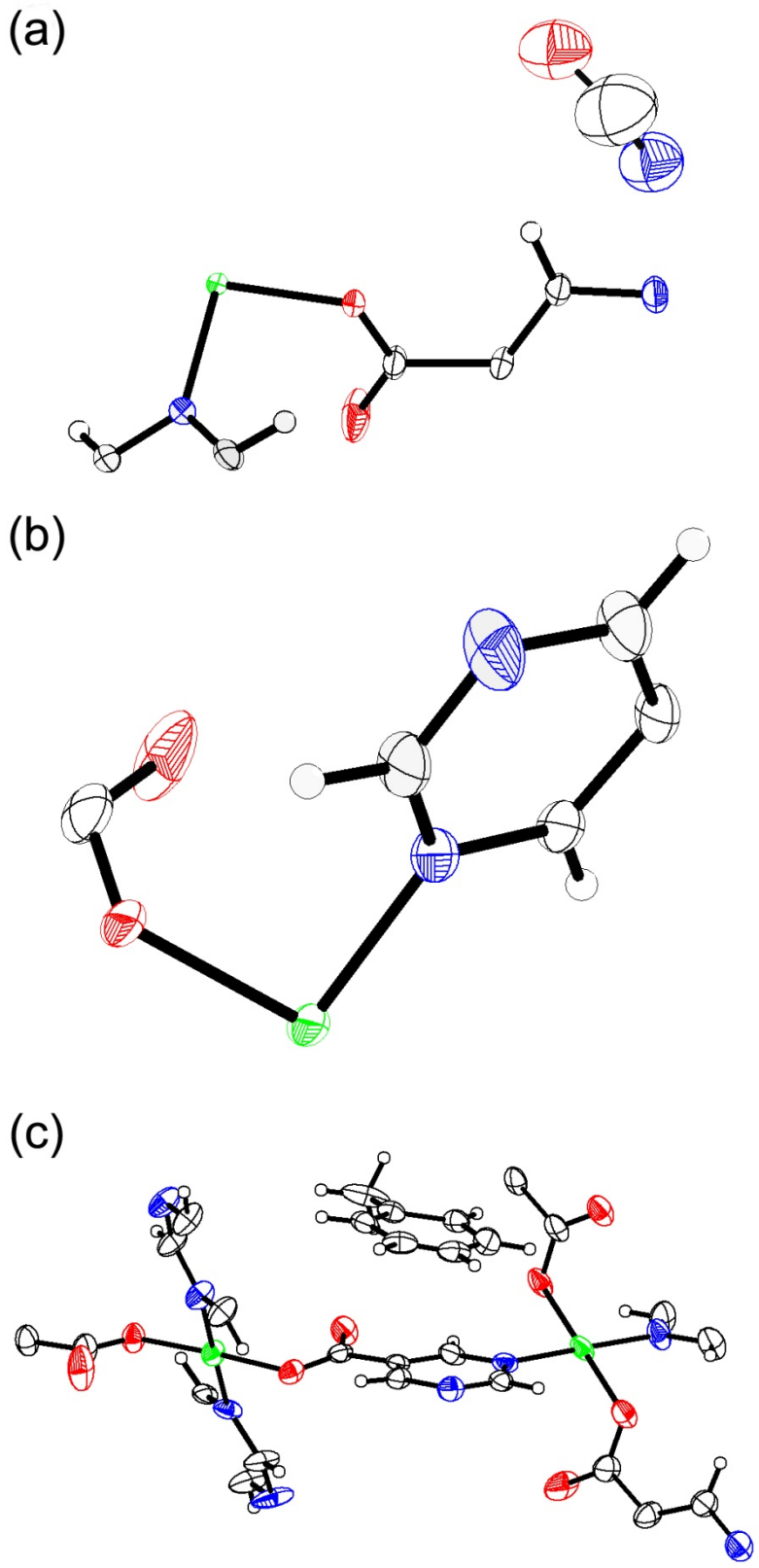

Figure S6. ORTEP view of **3**·DMF (a), **3** (b) and **3**·Toluene (c) shown with the 50% probability ellipsoids. Green, red and blue atoms are copper, oxygen and nitrogen, respectively.

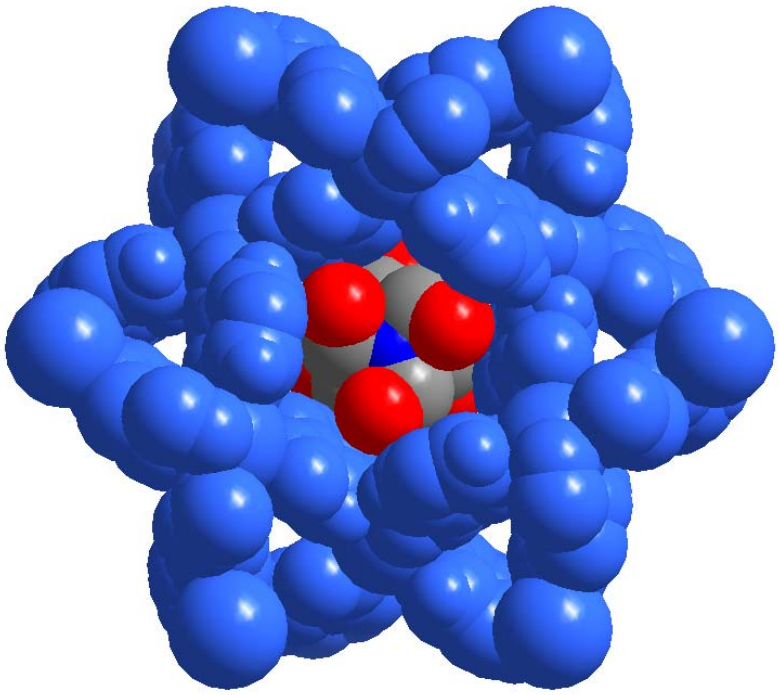

Figure S7. A partially expanded view of **3**·DMF showing the solvent molecules occluded in the channel. The DMF molecule is disordered over three positions and shown without hydrogen atoms.

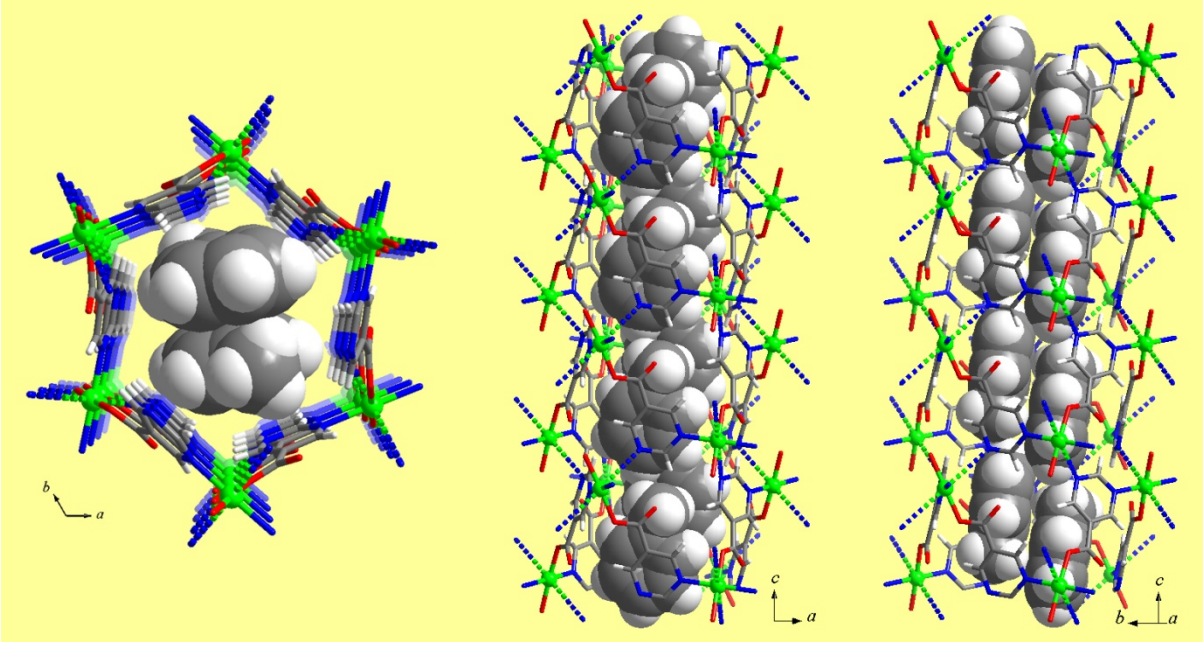

Figure S8. X-ray crystal structure of **3**·toluene showing the solvent molecules ordered inside the 1D channels. Broken lines represent the non-bonded interactions between interpenetrating nets.

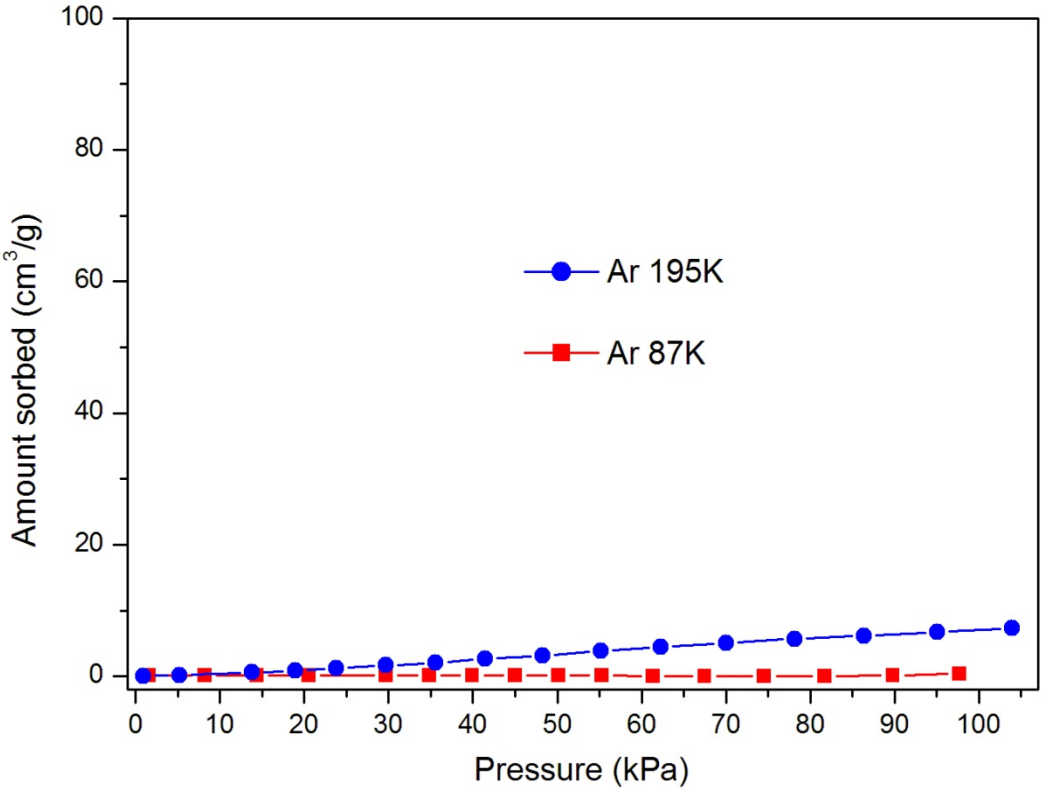

Figure S9. Ar sorption isotherms at 87 and 195 K.

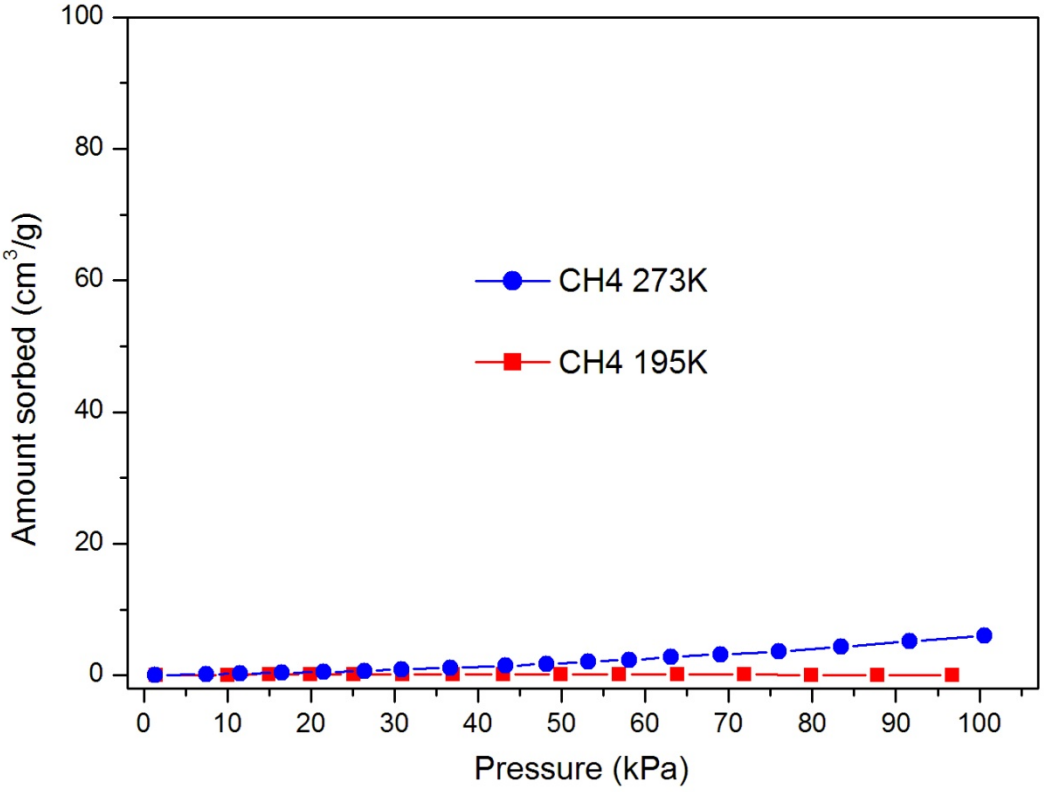

Figure S10. CH_4 sorption isotherms at 195 and 273 K.

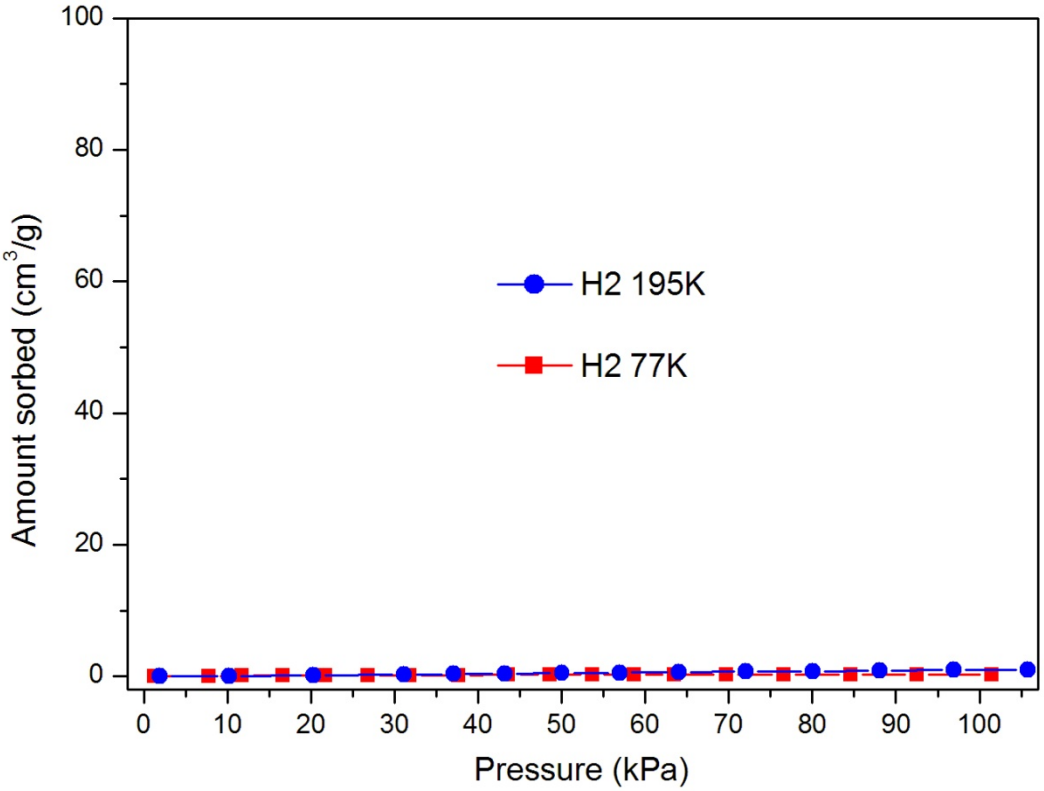

Figure S11. H_2 sorption isotherms at 77 and 195 K.

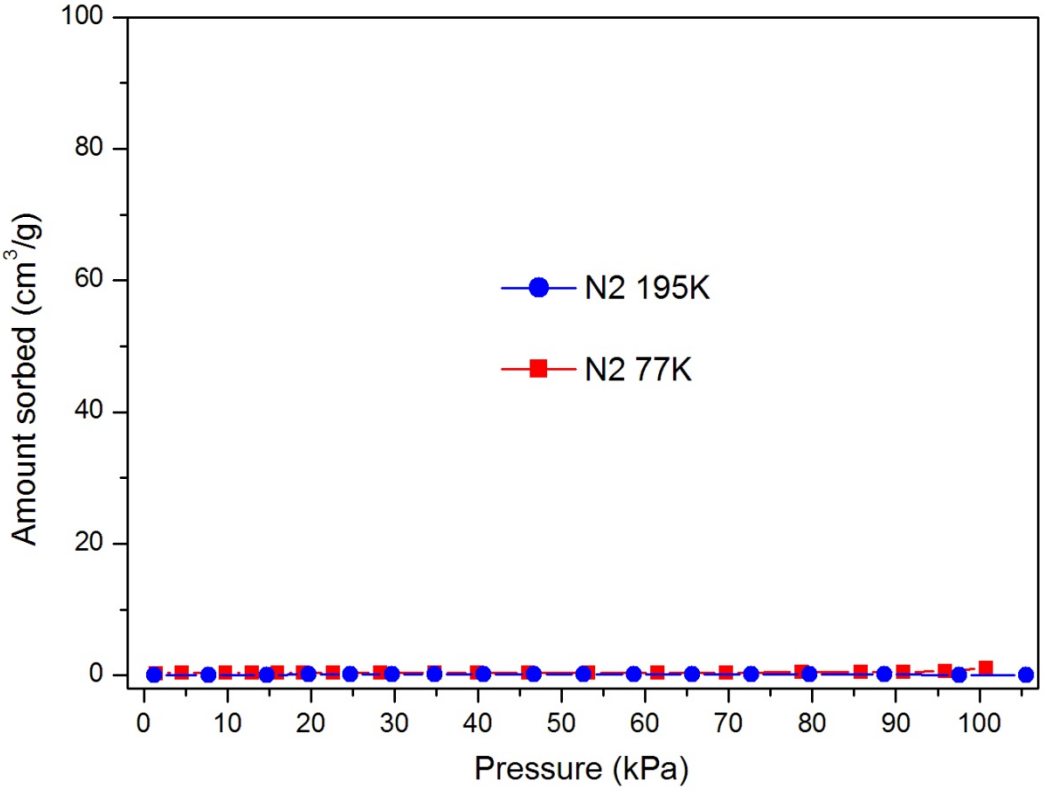

Figure S12. N_2 sorption isotherms at 77 and 195 K.

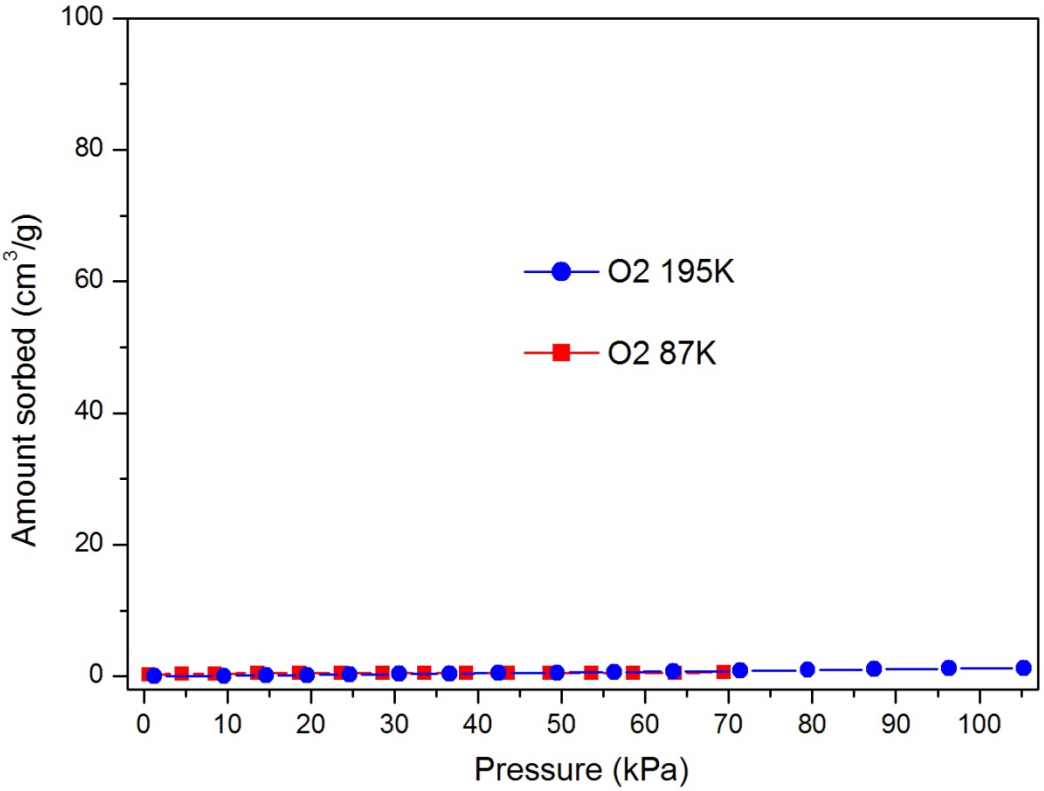

Figure S13. O_2 sorption isotherms at 87 and 195 K.