Electronic Supplementary Information for

High-symmetry hydrogen-bonded organic frameworks: air separation and crystal-to-crystal structural transformation

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Experiment Section

Materials and Physical Measurements. Reagents and solvents were commercially available and were used without further purification. Infrared spectra were obtained from KBr pellets on a Bruker Tensor 27 FT IR spectrometer in the 400–4000 cm^{-1} region. ^{1}H-NMR spectra were recorded on a Bruker AVANCE III 400MHz nuclear magnetic resonance spectrometer. Elemental analyses (C, H, N) were performed with a Vario EL elemental analyzer. PXRD patterns were recorded using a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα). TG analyses were performed using a TA Q50 and a NETZSCH TG 209 instrument with a heating rate of 5.0 °C/min under nitrogen.

Synthetic Procedures and Characterization.

1,3,5-triamino-2,4,6-trinitrobenzene (TATB) was synthesized according to the literature [D. Kim & I.-Y. Jeon, *et al*, *Synlett* **2012**, *24*, 246].

Benzo[1,2-d:3,4-d':5,6-d'']trisimidazole (**1**). A mixture of TATB (0.52 g, 2 mmol), sodium formate (8 g, 0.12 mol), Pd/C (0.1 g, 5 wt%, 0.05 mmol Pd) and formic acid (88%, 40 mL) were added and sealed into a Teflon reactor, the mixture was heated at 160 ^{o}C for 4 days. Upon completion, the cooled mixture was filtrated and the filtrate was treated with Na_2CO_3 until flocculent precipitate appeared. Then the precipitated solids were collected by filtration, rinsed with H_2O twice to give pale yellow powders. Afterwards, the powders were dissolved in NaOH (2 M, 10 mL), which was then neutralized by HCl (2 M). The resultant precipitate was collected by filtration, rinsed with H_2O twice, and dried under vacuum to provide fine powder of **1-H_2O** (yield: 60%). MS (EI) m/z = [M^+] 198. ^{1}H-NMR (300 MHz, DMSO-d_6 and HCl-d_1): δ (ppm) = 9.44(s, 3H). Anal. Calcd (%) for $C_9H_6N_6 \cdot 0.4H_2O$: C, 52.63; H, 3.34; N, 40.92. Found: C, 52.39; H, 3.19; N, 41.17. IR (cm^{-1}, KBr): 3163(m), 3072(s), 1629(s), 1478(m), 1387(s), 1264(s), 1188(w), 1018(m), 947(m), 888(m), 622(s), 448(m).

2,5,8-tris(trifluoromethyl)-4,7-dihydro-1H-benzo[1,2-d:3,4-d':5,6-d'']trisimidazole (**2**). The synthesis followed the literature procedure [L. Niedzicki, *et al*, *J. Power Sources* **2014**, *252*, 229] with slight modification. A suspension of TATB (2.1g, 8 mmol) and Pd/C (1 g, 5 wt%, 0.5 mmol Pd) in ethyl acetate (100 mL) was vigorously stirred at 70 ^{o}C under an H_2 atmosphere at 4 bar for 24 hours, then concentrated under reduced pressure, to which 1,4-dioxane (100 mL) and trifluoroacetic anhydride (10 mL) was successively added under N_2 atmosphere. The resultant suspension was further refluxed for 6 hours and filtered off to remove Pd/C after cooling to room temperature, and then concentrated hydrochloric acid (10 mL) was added to the filtrate. The reaction mixture was heated to 180 ^{o}C for 6 hours, and then concentrated to dryness. MeOH (100 mL) was added to dissolve the residue and a crude product precipitated from the solution after concentration (~20 mL). Then the precipitate was filtered off, washed with water to provide pale yellow powder. Finally, the crude product was sublimated

under reduced pressure to give white microcrystalline powder (yield: ~65%). The powder was dissolved in a mixed solvent of MeOH (6 mL) and water (1 mL), filtered, and then the filtrate was let stand and evaporated in air at room temperature. After 3 days, needle-like crystals of **2-H_2O** were filtered and washed by water, then dried in air (yield: ~70%). Anal. Calcd (%) for $C_{12}H_3F_9N_6 \cdot 7H_2O$: C, 27.28; H, 3.24; N, 15.91. Found: C, 27.10; H, 3.13; N, 16.22. IR (cm^{-1}, KBr): 3399(m), 3034(m), 1710(s), 1544(m), 1478(s), 1407(s), 1371(m), 1260(m), 1229(m), 1195(w), 1018(m),1149(m), 1001(s), 947(m), 753(s), 622(s), 522(m).

Crystal Structure Determination. Diffraction data were collected on a Rigaku R-AXIS SPIDER IP or Rigaku XtaLAB P300DS diffractometer by using graphite monochromated Mo and Cu Kα radiation, with absorption corrections applied by using multi-scan programs *PROCESS-AUTO* and *REQAB*, respectively. The structures were solved with the direct method and refined with a full-matrix least-squares technique with the *SHELXTL* program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms bonded to the O or N atoms were found from the nearby electron residue peaks, and others were generated by the riding mode. Crystal data as well as details of data collection and refinements are summarized in Table S1. CCDC 1445429–1445431 (**1-H_2O**, **2-H_2O** & **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Structure Refinement results.

Complex	**1-H_2O**	**2-H_2O**	**2**
Formula	$C_9H_6N_6{\cdot}xH_2O$[c]	$C_{12}H_3F_9N_6{\cdot}7H_2O$	$C_{12}H_3F_9N_6{\cdot}1/6C_{12}H_3F_9N_6$
Formula weight	200.00	528.31	469.24
Temperature (K)	117(2)	253(2)	173(2)
Crystal system	Trigonal	Orthorhombic	Cubic
Space group	*R*-3*m*	*Pbcn*	$P4_132$
a (Å)	12.657(4)	12.335(4)	15.843(2)
b (Å)	/	21.047(8)	/
c (Å)	9.296(3)	7.890(3)	/
V (Å^3)	1289.6(9)	2048(1)	3976(1)
Z	6	4	8
D_c (g cm^{-3})	1.545	1.713	1.568
reflns coll.	3722	16393	25167
unique reflns	325	1848	1226
Parameters	31	248	155
R_{int}	0.0577	0.0558	0.0338
R_1 [$I > 2\sigma(I)$][a]	0.0541	0.0514	0.0797
wR_2 [$I > 2\sigma(I)$][b]	0.1335	0.1247	0.2113
R_1 (all data)	0.0801	0.0551	0.0801
wR_2 (all data)	0.1549	0.1292	0.2114
Completeness	0.997	0.985	0.994
GOF	1.046	1.055	1.056
Flack	—	—	0.02(5)

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.
[c] Becuase the water molecule locates at an inversion center, $x <= 0.5$. TG and EA gave $x \approx 0.4$, while x was refined as 0.1 in the crystal structure to avoid very large thermal parameters.

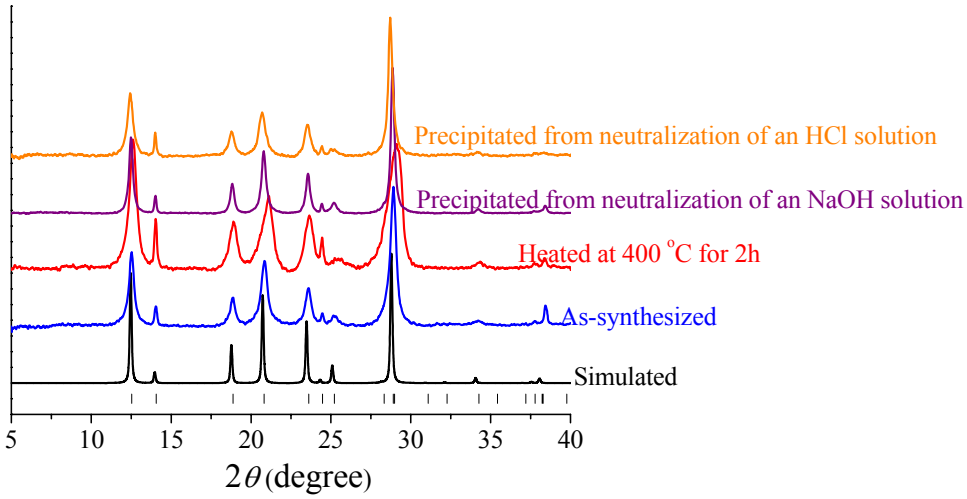

Fig. S1 PXRD patterns of **1-H_2O** after different treatments.

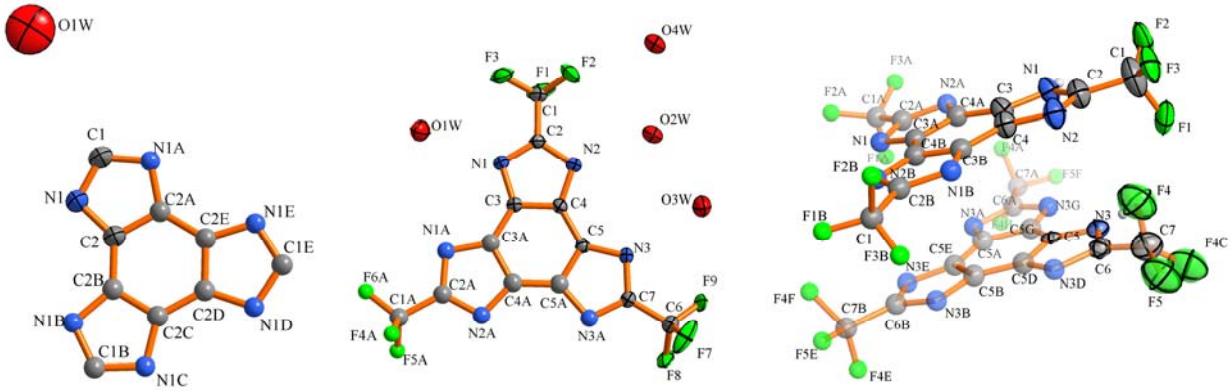

Fig. S2 The molecular structures of **1-H_2O** (left, symmetric codes: A: 1–*y*, 1–*x*, *z*; B: *x*, –1+*x*–*y*, *z*; C: 1–*y*, –1+*x*–*y*, *z*; D: 2–*x*+*y*, *y*, *z*; E: 2–*x*+*y*, 1–*x*, *z*), **2-H_2O** (middle, symmetric codes: A: 1–*x*, *y*, 3/2–*z*) and **2** (right, symmetric codes: A: 1/2+*z*, 1/2–*z*, –*y*; B: 1/2–*y*, –*z*, −1/2+*x*; C: 1–*z*, −1/2+*x*, 1/2–*y*; D: 5/4–*x*, 1/2+*z*, 1/2+*y*; E: 3/4–*z*, −1/2–*y*, 3/4–*x*; F: 1/4+*y*, 1/2–*x*, −1/4+*z*; G: 3/4+*y*, −3/4+*x*, 1/4–*x*; H: 1–*y*, −1/2+*z*, 1/2–*x*) (All H atoms are omitted for clarity).

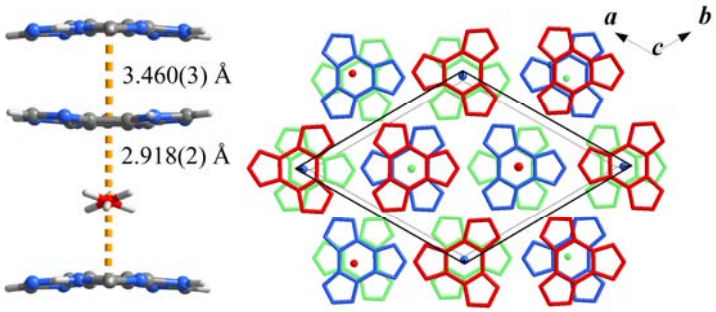

Fig. S3 The ABCABC··· array of π–π stacking interactions in **1-H_2O**.

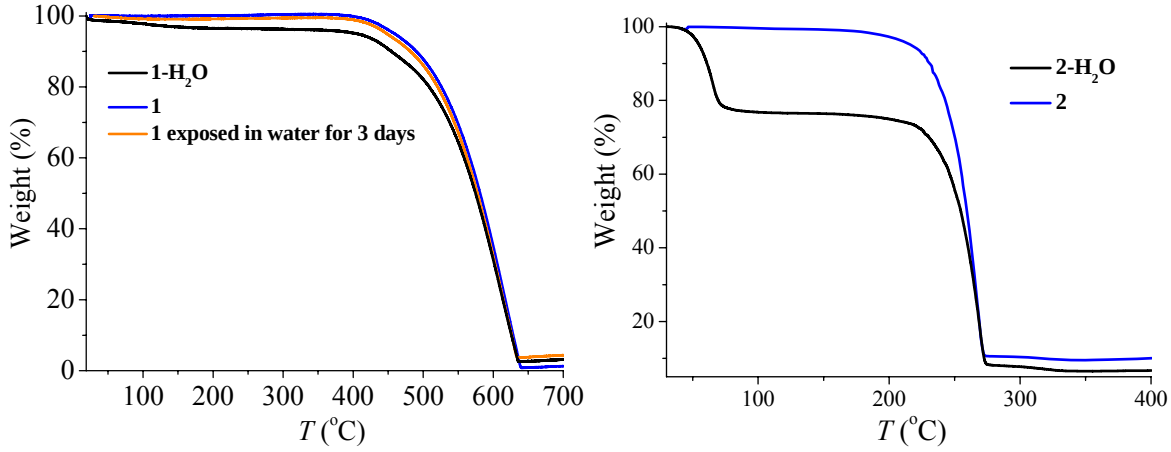

Fig. S4 TG curves of **1-H_2O**, **1**, **2-H_2O** and **2**.

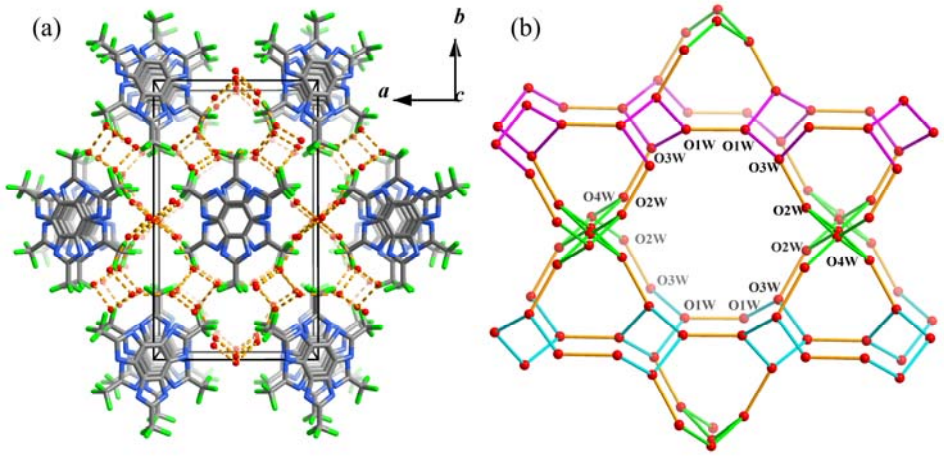

Fig. S5 (a) The 3D packing structure and (b) water network of **2-H_2O**.

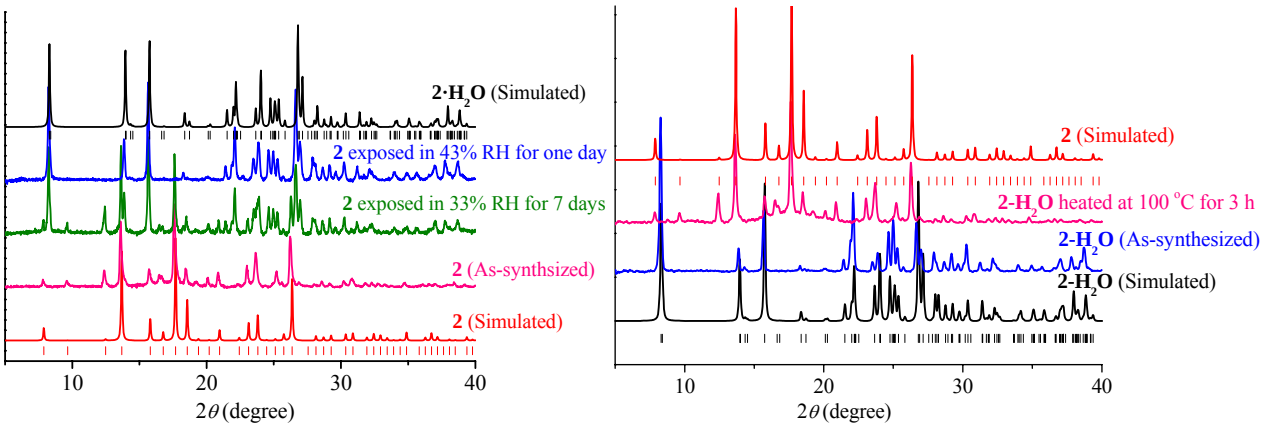

Fig. S6 PXRD patterns for **2** and **2-H_2O**, as well as their transformation.

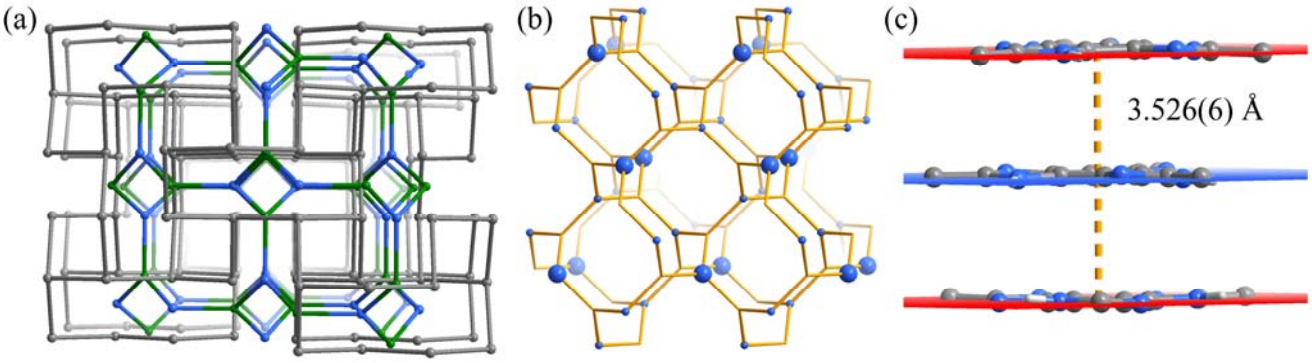

Fig. S7 (a) The topological representation of the host-guest structure (gray spheres and sticks are the molecules and double N-H···N hydrogen bonds constructing the hydrogen-bonded **srs** network, and the blue and green spheres are the aromatic cores and CF_3 groups of the hydrogen-bond free molecules occupying the **srs-b** channel, respectively), (b) a possible channel topology considering that one third of cavities are completely occupied by the molecule (occupied and unoccupied sites are shown as large and small blue spheres respectively), and (c) the sandwich configuration of π–π stacking between the host (red) and guest (blue) molecules (F atoms are omitted for clarity) in **2**.

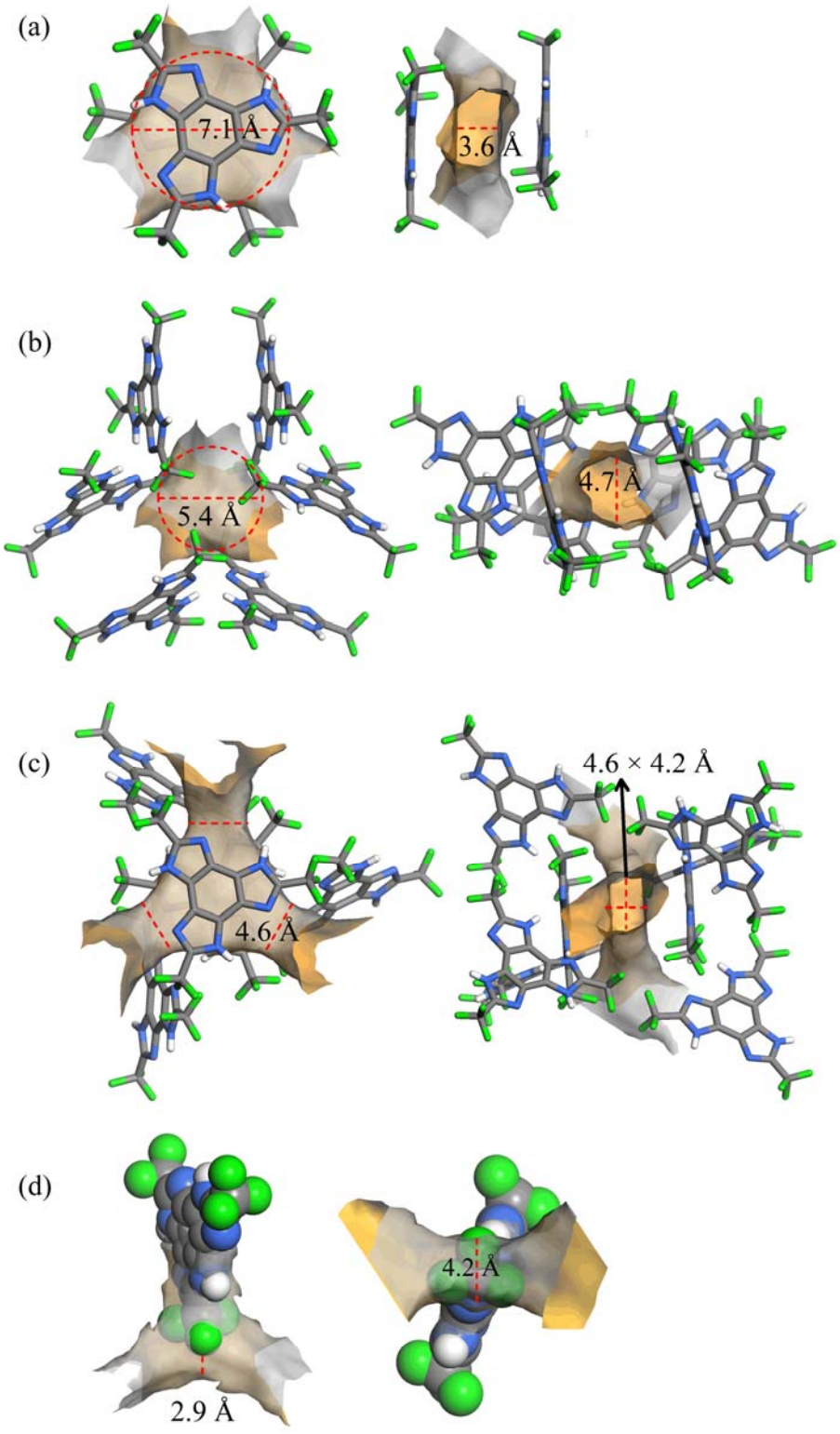

Fig. S8 The sizes of (a) the disc-shaped cavities, (b) the ellipsoidal cavities, (c) the aperture without and (d) with guest in **2**.

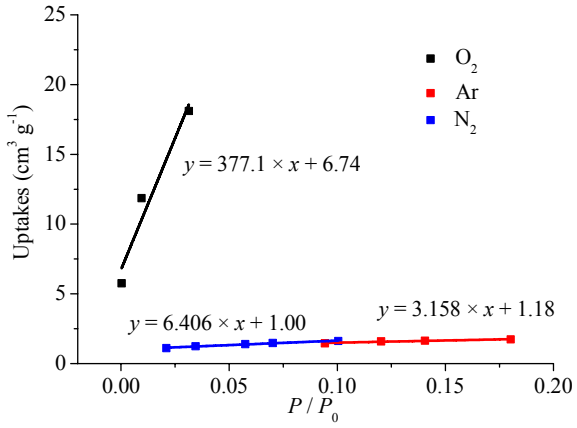

Fig. S9 The Henry's constants of O_2, Ar, and N_2 adsorption isotherms for **2** measured at 77 K.