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Supporting Information

A Biporous Coordination Framework with High H_2 Storage Density

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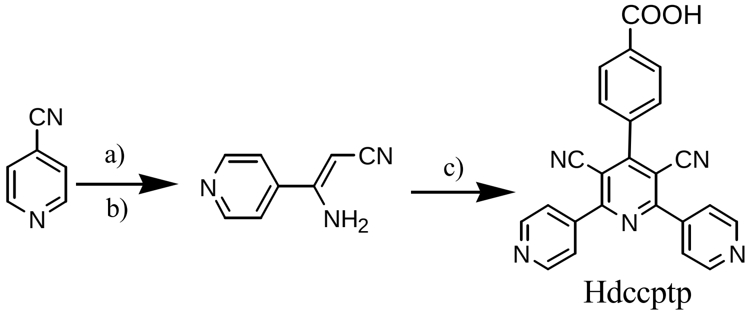
Experimental section

Elemental analyses of C, H and N were performed by the Elemental Analysis Service of the School of Chemistry, University of Nottingham. Infrared spectra were measured as KBr disks on a Nicolet Avatar 360 FT-IR system over the 400-4000 cm^{-1} range. Thermal gravimetric analysis was performed on a Rheometric Scientific STA 1500H thermal analyzer at a heating rate of 1ºC/min^{-1}. X-ray powder diffraction data were collected on a Philips X'pert powder diffractometer with Cu K_{α} radiation from samples mounted on the flat glass plate sample holder. Scans of approximately 90 min were run for each sample over the range $5^{o} \leq 2\theta \leq 60^{o}$ with a step size of 0.02^{o} in 2θ. Simulated powder patterns were generated with POWDER CELL software[1] from CIF data of final single-crystal structural refinement.

Materials and synthesis; 4-cyanoyridine, 4-formylbenzoic acid, potassium tert-butoxide, and $Cu(NO_3)_2 \cdot 2.5H_2O$ were purchased from the Aldrich Chemical Co. and used as received without further purification.

3,5-Dicyano-4-(4-carboxyphenyl)2,2':6'4''-terpyridine (Hdccptp) was prepared from β-amino-β-(pyrid-4-yl)acrylonitrile and 4-carboxybenzaldehyde in acetic acid (Scheme 1), whilst the acrylonitrile was prepared by a modification of Yamagushi's method.[2] β-amino-β-(pyrid-4-yl)acrylonitrile, $C_8H_7N_3$: elemental analysis (found/calcd): C, 66.15/66.19; H, 4.83/4.86; N, 28.94/28.95; IR (KBr, ν_{max}): 3335, 2193 cm^{-1}; m/z 146.15 (MH^+); ^{1}H-NMR (DMSO-d_6): 8.63 (d, 2H), 7.57 (d, 2H), 7.02 (d, 2H), 4.40 (s, 1H).

Hdccptp, $C_{24}H_{13}N_5O_2$: elemental analysis (found/calcd): C, 71.88/71.46; H, 3.33/3.25; N, 17.67/17.36; IR (KBr, ν_{max}): 3038, 2225 cm^{-1}; m/z 406.2 $(MH_3)^{3+}$ (100); 379.3 (80%); ^{1}H-NMR (DMSO-d_6): 8.77(d, 4H), 8.19 (d, 4H), 7.95 (d, 2H) and 7.75 (d, 4H).



Scheme S1. Synthesis of the ligand Hdccptp: a) CH_3CN, benzene, t-BuOH; b) $NaHCO_3$; c) 4-carboxybenzaldehyde, CH_3COOH, 120°C.

*Preparation of [[Cu(dccptp)(NO$_3$)]·0.5MeOH·0.5dioxane (**1**)*: Single crystals of **1** were grown by solvothermal reaction of equimolar amounts of $Cu(NO_3)_2 \cdot 2.5H_2O$ and Hdccptp in methanol and dioxane at 100°C for 84 h. Green tablets were isolated, washed with MeOH and air-dried to give **1** (76% yield based on $Cu(NO_3)_2 \cdot 2.5H_2O$). Elemental analytical and TGA correspond to [[Cu(dccptp)(NO_3)]·0.5MeOH·0.5dioxane：calc: C, 54.13, H; 3.09; N, 14.29; found: C, 54.21, H; 3.11; N, 14.35. ν_{max} [KBr]: 3446, 3047, 2360, 2340, 1699, 1652, 1635, 1558, 1540, 1507, 1497, 1474, 1457, 1384, 1221, 1068, 850, 800, 706, 668 cm^{-1}.

Single crystal X-ray diffraction analysis

Suitable crystals were glued to glass fibres and mounted on a Bruker SMART1000 CCD diffractometer equipped with an Oxford Cryosystems open-flow cryostat and graphite monochromated Mo-$K\alpha$ radiation (λ = 0.71073Å). Crystallographic data were collected at 150 K, and an empirical absorption correction by SADABS[3] was applied to the intensity data. All calculations were performed with the SHELXTL program. The structure was solved by direct methods using SHELXS97,[4a] successive Fourier difference synthesis, and refined by full-matrix squares on F^2 using SHELXL97,[4b] with anisotropic thermal parameters for all non-hydrogen atoms on coordination framework. Hydrogen atoms on ligand and dioxane were placed in calculated positions and refined using a riding model, while those on methanol were found from the difference Fourier map and then refined using a riding model. Disorder of the cyano groups was modelled by

allowing two alternative positions for each C and N atom. The final refined occupancies were: C13/N2 0.647(8) and C13'/N2' 0.353(8); C14/N3 0.545(7) and C14'/N3' 0.455(7). The following distance restraints were applied to the disordered cyano groups:
DFIX 1.14 0.01 C13 N2 C13' N2' C14 N3 C14' N3'
DFIX 1.45 0.01 C13 C12 C13' C12 C14 C9 c14' C9
DFIX 2.59 0.02 C12 N2 C12 N2' C9 N3 C9 N3'

The following distance restraints were applied to the dioxane molecules:
DFIX 1.45 0.01 O7 C26 O7 C29 O8 C27 O8 C28
DFIX 1.55 0.01 C26 C27 C28 C29.

The assignment of the C and O atoms in the methanol molecule was carried out by competitive refinements. In the model we present, both atoms have similar and reasonable U_{iso} values of about 0.10 Å^2. Reversing the assignment leads to residuals which are only slightly higher but the U_{iso} values for these two atoms diverge and at convergence differ by a factor of three. The value for the “O” atom is 0.174(7) Å^2 while that of the “C” atom is 0.057(3) Å^2, strongly suggesting that this assignment is incorrect. Despite the validation problems with our model, we prefer it to the alternative but accept that the true situation in the crystal may be more complex.

*Crystal data for **1***. $C_{26.50}H_{18}CuN_6O_{6.50}$, M = 588.01, monoclinic, space group $C2/c$, a = 12.2342(11), b = 25.093(2), c = 19.6064(18) Å, β = 104.225(2), V = 5834.4(9) Å^3, Z = 8, T = 150(2) K, μ(Mo-$K\alpha$) = 0.799, R_1 = 0.080, wR_2 = 0.216, the maximum peak: 1.15 eÅ^{-3}; 15057 reflections measured, 5275 unique (R_{int} = 0.046) which are used in all calculations.

A SQUEEZE calculation in PLATON[5] was used to confirm the solvent content, returning a total of 270.4 solvent electrons per unit cell, which corresponds to 0.5 MeOH and 0.5 dioxane per formula. This is consistent with the above refinement involving solvent molecules. Although refinement using the .hkp created by PLATON SQUEEZE as the new .hkl leads to lower residuals (R_1 = 0.0639, wR_2 = 0.154) and a lower $\Delta\rho_{\mathrm{max}}$ of 0.72 eÅ^{-3}, we elected to publish the structure incorporating the solvent molecules.

Sorption isotherm measurement of complex 1

The out-gassing and isotherm measurements were performed on a Hiden Isochema (Warrington UK.) Intelligent Gravimetric Analyzer (IGA) equipped with a micro-gram balance, 2mbar, 100mbar and 20bar pressure transducers and a Hüber ministat circulating water bath. For measurements at liquid nitrogen temperature, a standard low-temperature liquid Dewar vessel was used. Before gas absorption measurement, the sample was activated at 125°C under high vacuum (10^{-8} mbar) for 20 hours. All isotherm data points were fitted by the IGASwin system software v.1.03.143 (Hiden Isochema, 2004) using a linear driving force model when > 98% equilibration had been reached. All changes in sample weight were corrected for buoyancy effects.

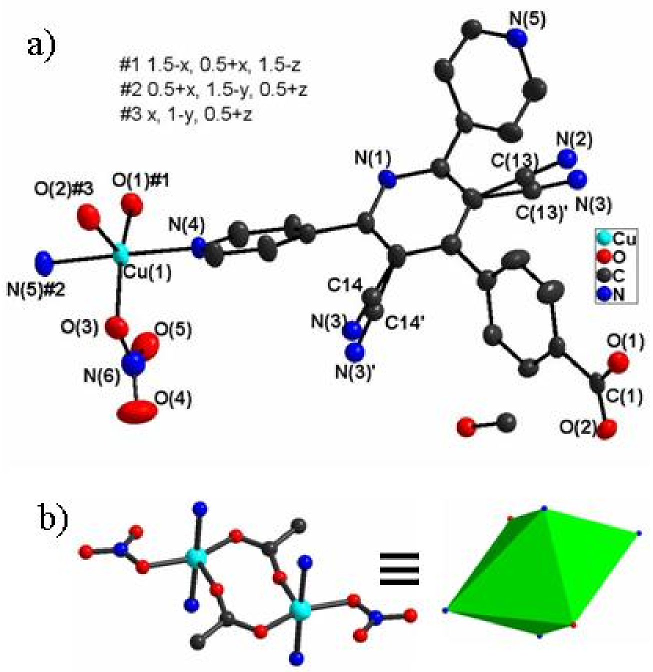


Figure S1: (a) Asymmetric unit of **1** with atom labelling (both disordered sites of the cyano groups are shown); (b) the localized geometry of the 6-connected binuclear {Cu_2} building-block in **1**.

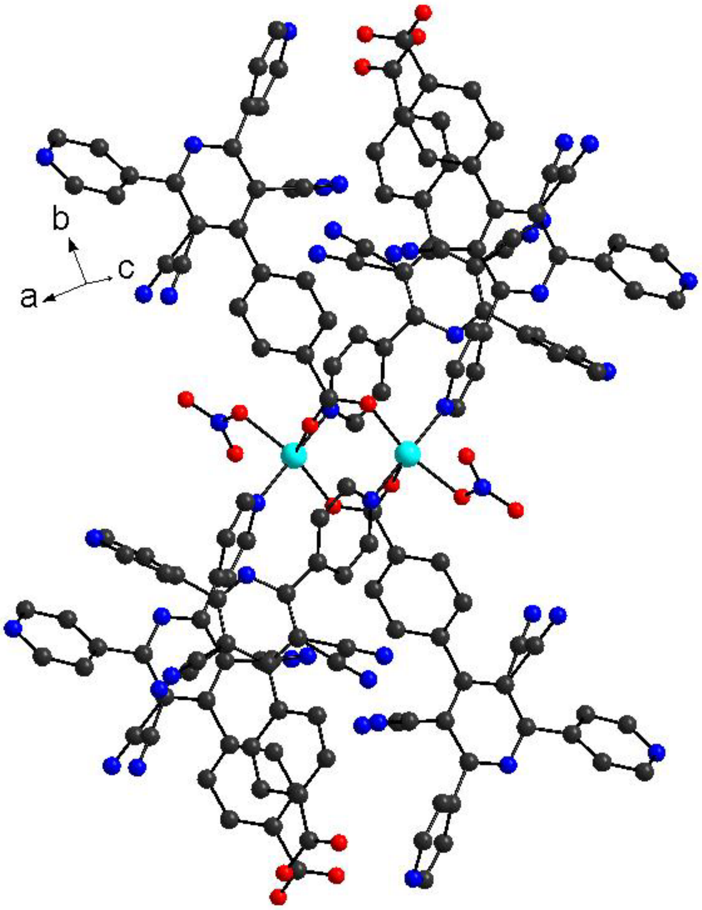
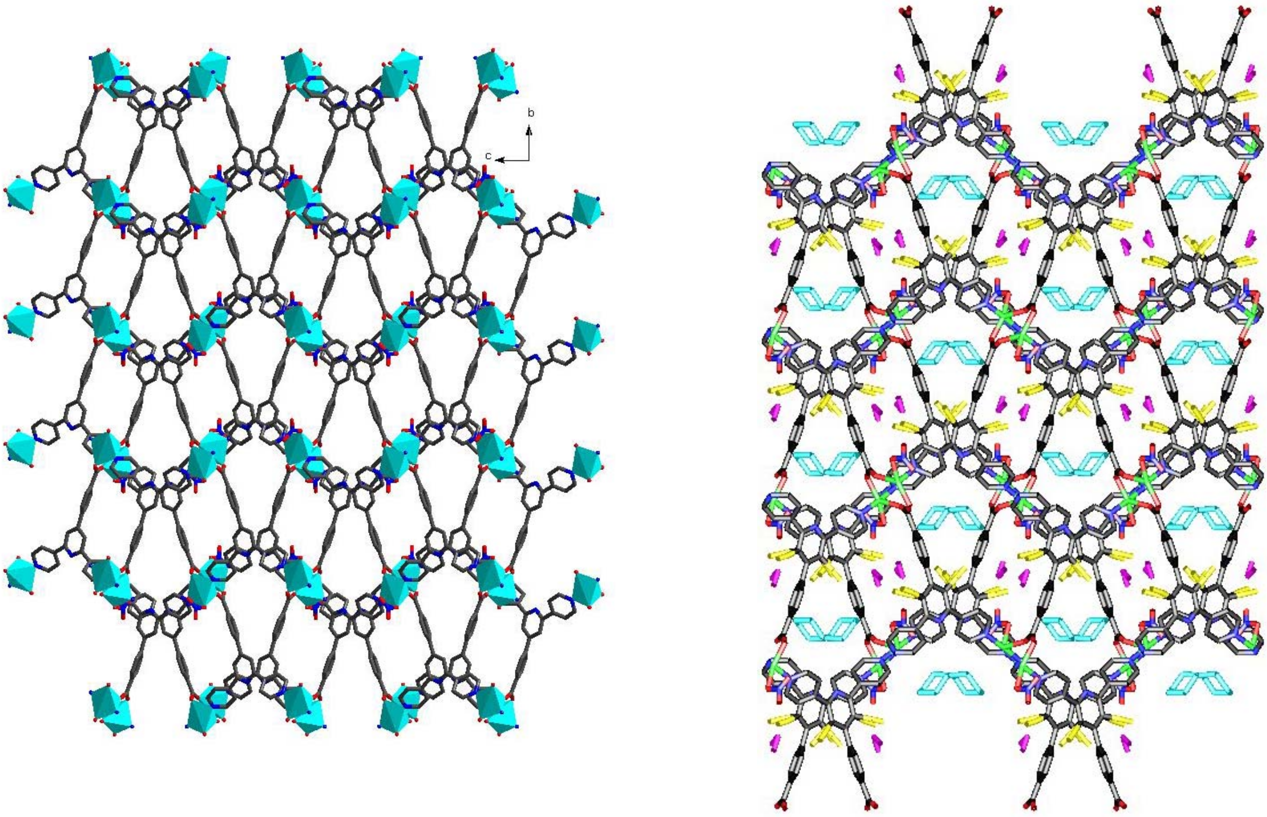


Figure S2: Perspective view of the binuclear copper(II) building blocks. Atoms are identified by colour as follows: Cu, pale blue, O, red; N, blue; C, black. H atoms are omitted for clarity.



(a)

(b)

Figure S3: a) A view of the three-dimensional (3,6)-connected coordination framework of **1** showing the two distinct channels. All H atoms omitted for clarity; b) biporous channels containing 1,4-dioxane and MeOH guests from a mixture of the two solvents (methanol, purple; dioxane, cyan; cyano groups, yellow; C, gray; N, blue; O, red; and Cu, green).

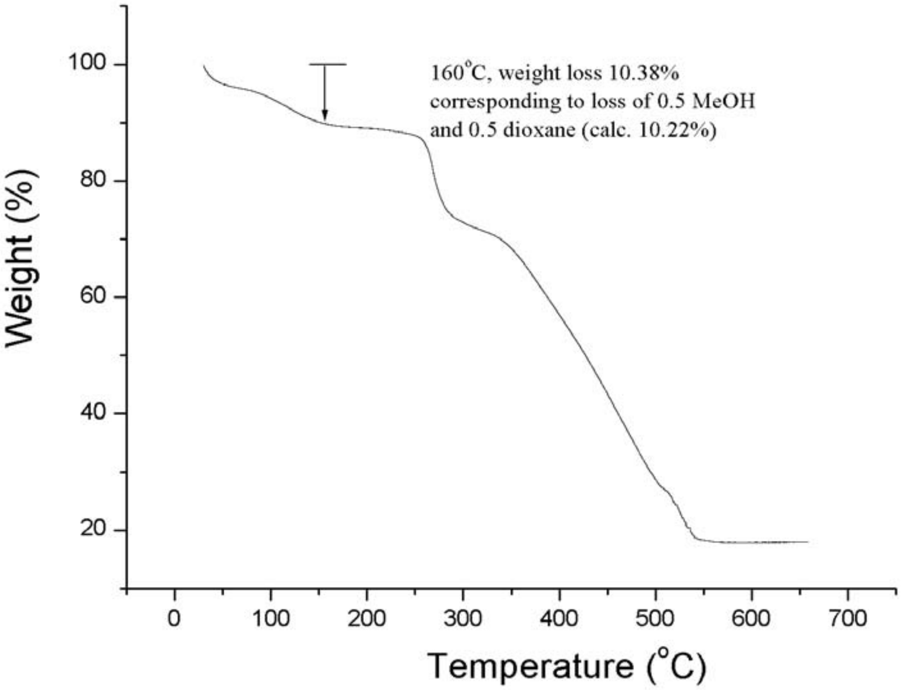


Figure S4: TGA trace for 1 under a flow of N_2 at room pressure

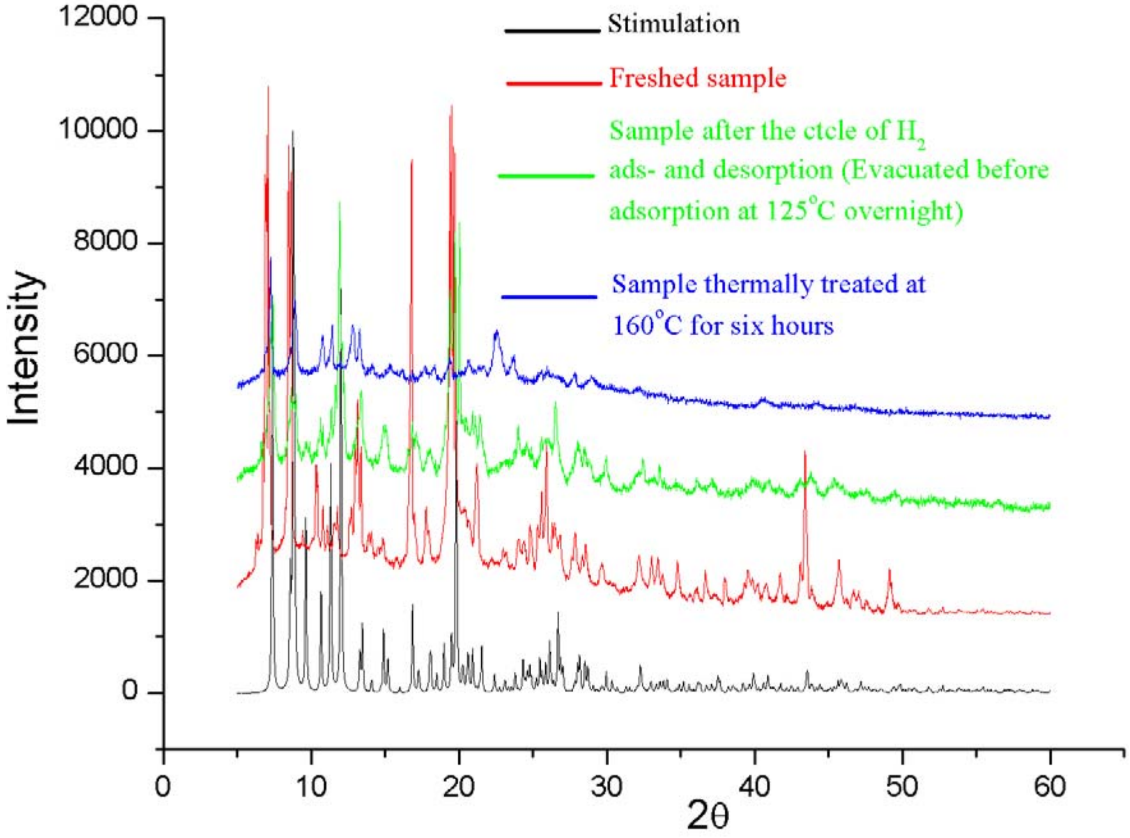
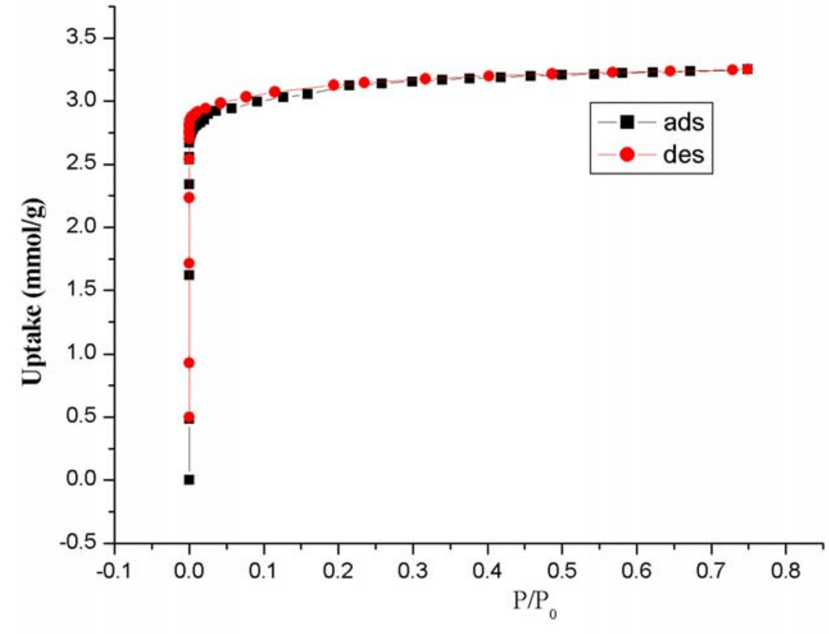


Figure S5: Powder X-ray diffraction patterns of **1** following thermal treatment**.**



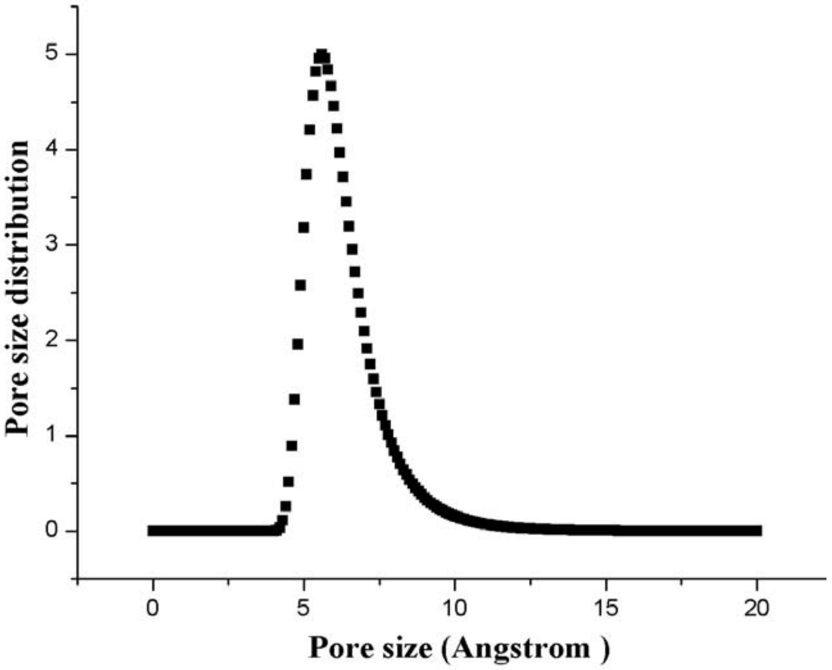


Figure S6: a) N_2 sorption isotherm **2**; b) pore distribution determined by Dubinin-Astakhov (DA) equation, using N_2 sorption data;

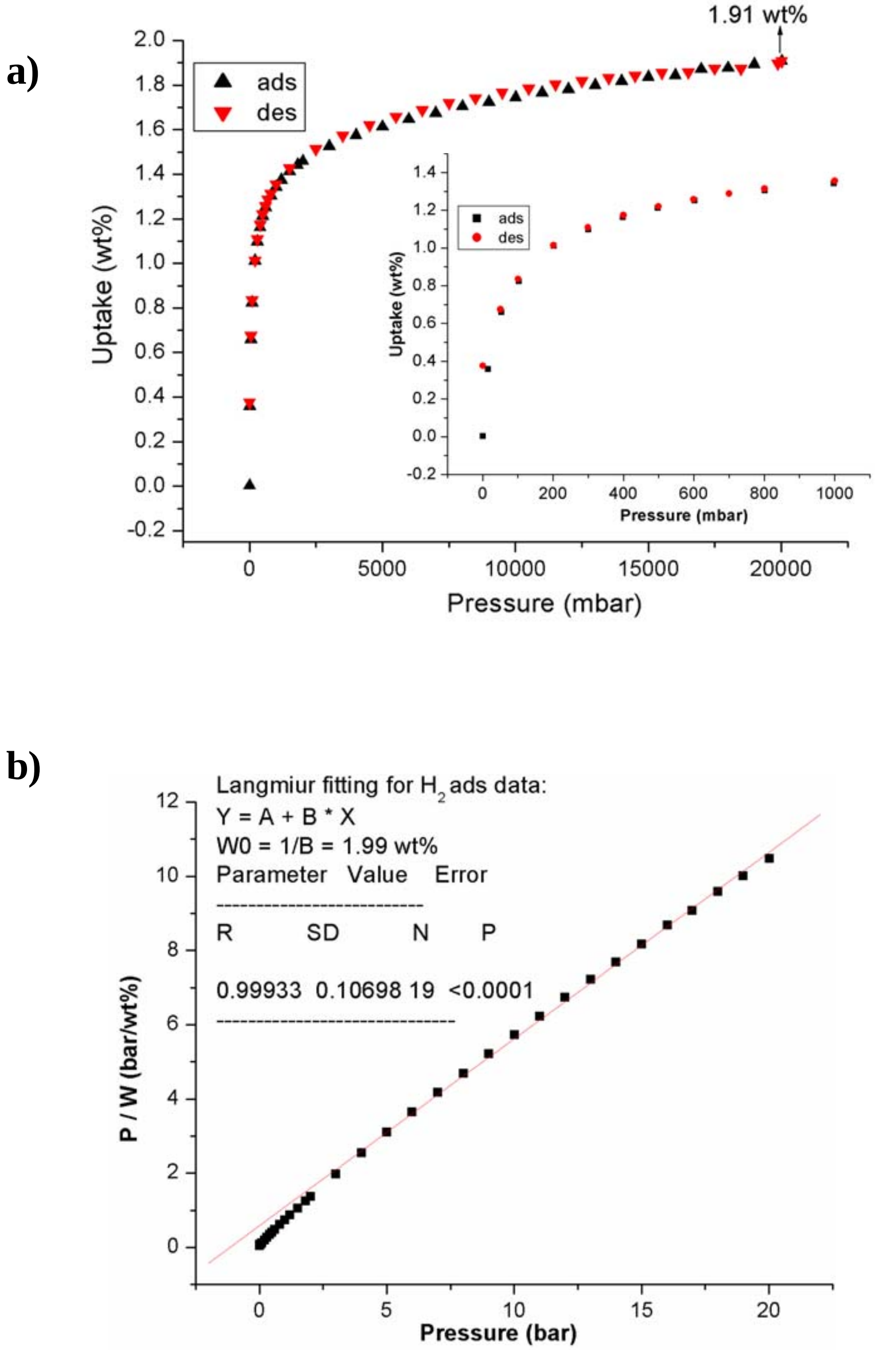
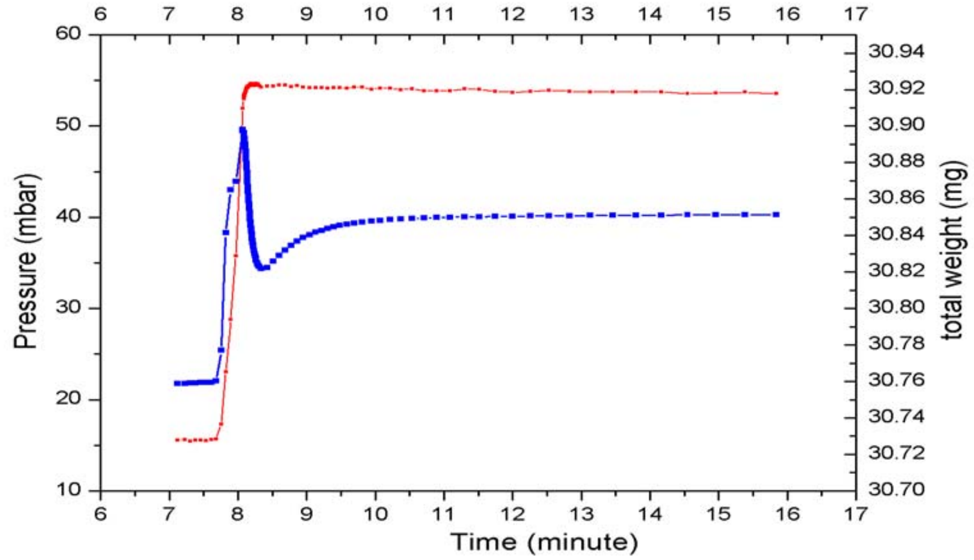
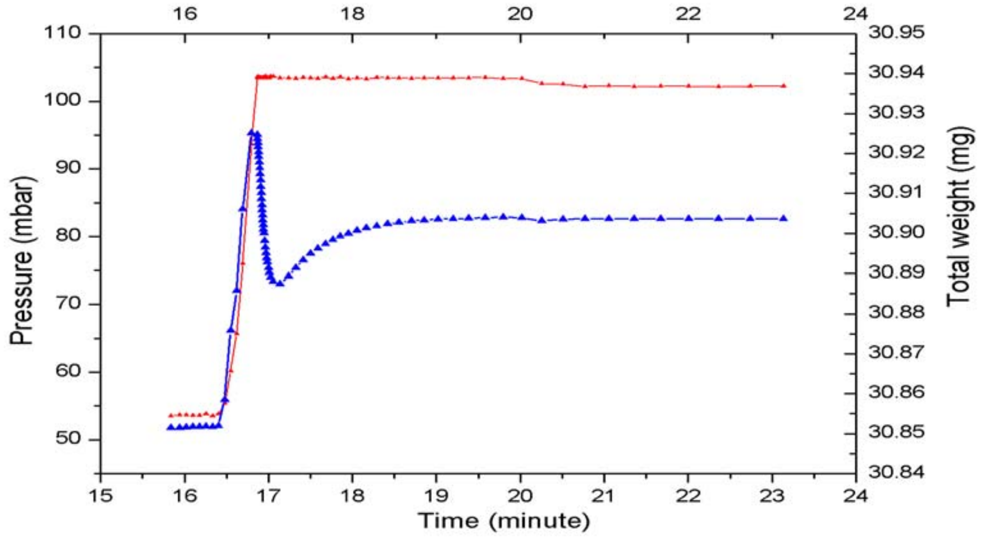


Figure S7: a) H_2 sorption isotherm of **2** at 77K, the insert is an enlargement of the low-pressure region; b) Langmuir linear fitting of H_2 sorption.

A Langmuir plot was used to estimate the maximum uptake of hydrogen at 77K. $P/W = (1/W_o)*P + 1/(W_o*K)$, $W_o = 1/B$, where W is the degree of sorption at the pressure of P, W_o is the saturated adsorption and K is a coefficient.


6
7
8
9
10
11
12
13
14
15
16
17
60
50
40
30
20
10
Pressure (mbar)
30.94
30.92
30.90
30.88
30.86
30.84
30.82
30.80
30.78
30.76
30.74
30.72
30.70
total weight (mg)
Time (minute)


16
18
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Pressure (mbar)
30.95
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30.90
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30.88
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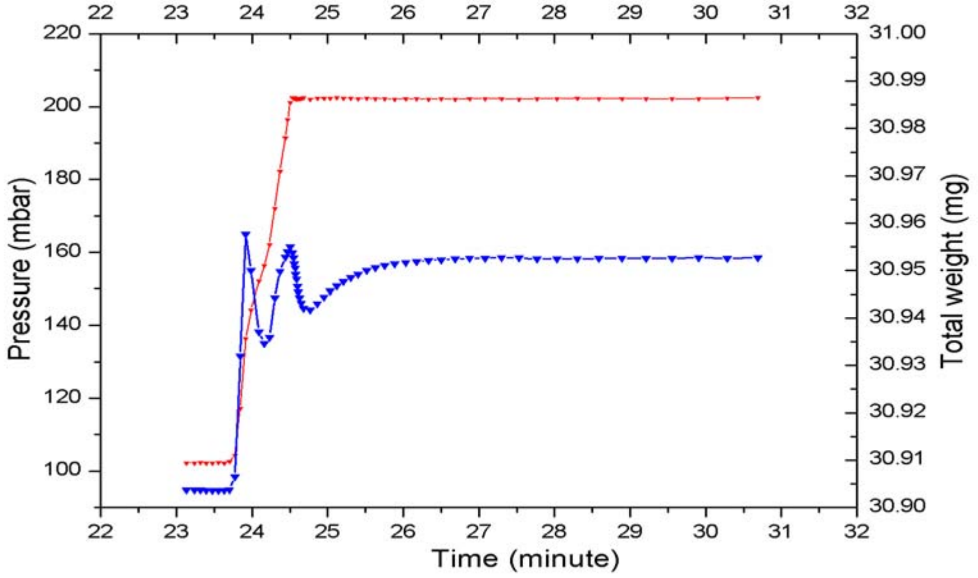
Time (minute)


22
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31
32
220
200
180
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140
120
100
Pressure (mbar)
31.00
30.99
30.98
30.97
30.96
30.95
30.94
30.93
30.92
30.91
30.90
Total weight (mg)
Time (minute)

Figure S8: Kinetic equilibrium of hydrogen absorption of **2**, at 50 (top), 100 (medium) and 200 mbar (bottom) pressure step, respectively. Pressure, red; and total weight, blue.

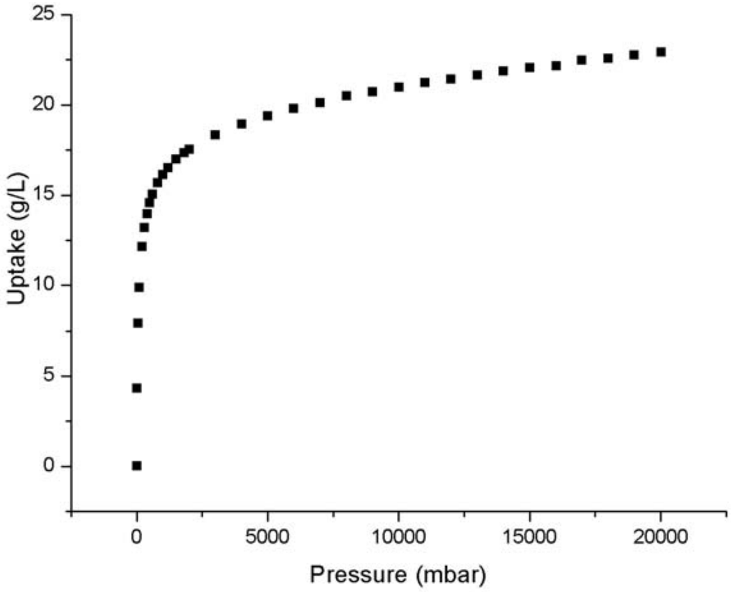

Figure S9: Volumetric hydrogen adsorption by **2** at 77K.

The Dubinin-Radushkelvich (DR) equation $[\ln(W_0/W)]^{1/2} = (RT/\beta E_0)(\ln(P_0)-\ln(P))$ was converted to the form of Y = A + BX:

$RT\ln(P) = RT\ln(P_{0q}) - \beta E_0[\ln(W_0/W)]^{1/2}$

where W_0 is the estimated maximum uptake obtained from Langmiur plot, P_{0q} represents the saturated vapour pressure of quasi-vaporized supercritical gas, and βE_0 is the adsorption energy. Dubbinin-Radushkevich (DR) analysis gave an estimate of the adsorption energy βE_0, and the isosteric heat of hydrogen adsorption at the fraction filling of $1/e$ was obtained from:

$q_{st,\,\Phi=1/e} = \Delta H_v + \beta E_0$

where ΔH_v is the heat of vaporization of H_2, $\Delta H_v = 0.92$ kJ mol^{-1}

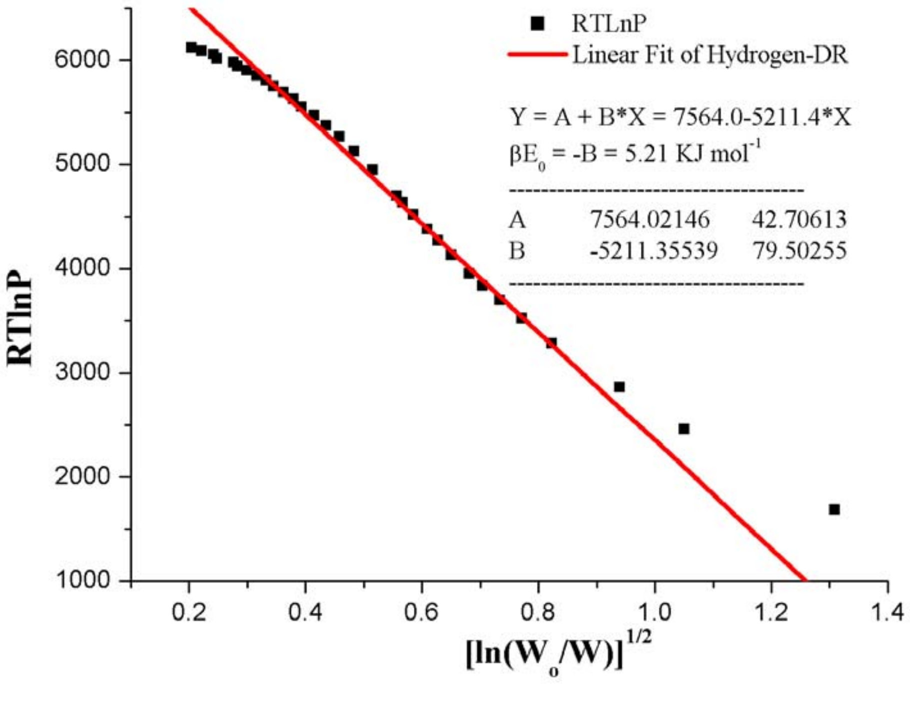

Figure S10: Linear Fit of H_2 uptake by DR analysis

Table S1 Summary of hydrogen adsorption in MOFs at 77K[a]

Materials[a]	D_{calcd} [g/cm^3]	S_p[b, c, d] [Å]	SA [e] [m^2/g]	F_{AV} [i] [%]	V_{PLAT} [cm^3/g]	V_{P} [cm^3/g]	N_{H2} [wt%]	D_{H2} [j] [×10^{-2} g/cm^3]	$N_{\mathrm{H2-psa}}$ [×10^{-3} wt% m^{-2} g]	P_c	$D_{\mathrm{H2-V}}$[l] [g L^{-1}]	Ref.
2	1.202	5.5	268	31.4	0.261	0.113	1.01 / 1.34 / 1.91	3.87 / 5.13 / 7.32[k]	3.77 / 5.00 / 7.13	0.2 / 1 / 20 bar	23.9	This work
$Mn(HCO_2)$	–	3/4.7	297[f]	33	–	–	0.9	–	3.03	1 atm	–	[6]
$Mg_3(ndc)_3$	–	≈ 3.5	190[g]	–	–	–	0.48	–	2.53	1.17 bar	–	[7]
$Sc_2(bdc)_3$	–	≈ 5.3	721	–	–	0.33	1.5	4.55	2.08	0.8bar	–	[8]
MIL-102	–	≈ 4	42	–	–	0.12	0.9	7.5	21.43	10 bar	–	[9]
MOF-5	0.590	11.2	2296	0.59	–	1.19	0.60 / 1.16 / 4.75	0.50 / 0.97 / 3.99	0.26 / 0.51 / 2.07	0.5 / 1 / 20 bar	28.0	[10], [11], [12]
IRMOF-6	0.653	9.3	2804	0.50		1.14	0.61 / 1.19 / 4.50 / 4.85	0.54 / 1.04 / 3.95 / 4.25	2.17 / 0.42 / 1.60 / 1.73	0.4 / 1 / 20 / 50 bar	31.6	[10], [13]
IRMOF-11	0.760	9	1984	0.40		0.68	0.58 / 1.51 / 3.43 / 3.52	0.85 / 2.22 / 5.04 / 5.17	2.92 / 0.76 / 1.73 / 1.77	0.2 / 1 / 20 / 50 bar	26.8	[10], [11]
IRMOF-20	0.511	14	4024	–	–	1.53	0.80 / 1.30 / 5.27 / 6.70	0.52 / 0.84 / 3.44 / 4.38	0.20 / 0.32 / 1.31 / 1.67	0.7 / 1.3 / 20 / 70 bar	34.2	[10], [11]
MOF-177	0.427	11/17	4746	0.63	–	1.59	0.99 / 6.08 / 7.52	0.62 / 3.82 / 4.73	0.21 / 1.28 / 1.58	0.9 / 20 / 70 bar	32.1	[10], [13]
MOF-74	1.22	–	950	–	–	0.39	1.02 / 1.36 / 2.24 / 2.26	2.61 / 3.48 / 5.74 / 5.79	1.07 / 1.43 / 2.36 / 2.38	0.2 / 1 / 20 / 26 bar	27.6	[10], [14]
MOF-505	–	6.7/8.3/10.1	1830[h]	37	–	0.63	2.47	3.94	1.35	1 atm	–	[15]
$Cu_2(bptc)$	0.927	6.5	1670	63.3	0.683	0.680	2.59 / 4.02	3.81 / 5.91	1.55 / 2.41	1 / 20 bar	38.9	[16]
$Cu_2(tptc)$	0.650	7.3	2247	70.4	1.083	0.886	2.52 / 6.06	2.84 / 6.84	1.12 / 2.70	1 / 20 bar	43.6	[16]
$Cu_2(qptc)$	0.587	8.3	2932	75.5	1.284	1.138	2.24 / 6.07	1.97 / 5.33	0.76 / 2.29	1 / 20 bar	41.1	[16]
$Ni_3(OH)(dcppy)_3$	–	10	1553	–	–	–	1.99 / 4.15	–	1.28 / 2.67	1 / 20 bar	–	[17]

[a] Acronyms and abreviation: D_{calcd}, S_p, SA and F_{AV} are the calculated density with all guests removed, the pore size, the surface area and the accessible volume fraction, respectively. V_{PLAT} represents the calculated pore volumes using PLATON, and V_p is the measured pore volume from N_2 isotherms. N_{H2} is the amount of H_2 absorbed at 77 K; D_{H2} is the absorbed H_2 density; $N_{\mathrm{H2-PSA}}$ is the absorbed H_2 per surface area; P_c is the pressure conditions corresponding to the above N_{H2}, while $D_{\mathrm{H2-V}}$ is the volumetric density of H_2 adsorbed. ndc = naphthalene-2,6-dicarboxylate; bdc = benzene-1,4-dicarboxylate; bpdc = biphenyl-3, 3’:5,5’-tetracarboxylate; tptc = terphenyl-3,3”:5,5”-tetracarboxylate; qptc = quatephenyl 3,3’”:5,5’”-tetracarboxylate； dcppy = 3,5-Di(4-carboxyphenyl)pyridine. [b] determined from N_2 sorption at 77K. [c] Calculated using the Cerius2 software package. Crystallographic data for the evacuated framework were used where available.[d] Free diameters corresponding to the largest spheres that can pass through the apertures of the frameworks. [e] Calculated for N_2 absorption data collected at 77K using BET model except where indicated. [f] BET surface area for CO_2 at 195 K. [g] Calculated from O_2 adsorption data collected at 77K by using BET model. [h] Langmuir surface area from N_2 at 77K. [i] Calculated using PLATON/SOLV. [j] Calculated from the absorbed H_2 values (N_{H2}) and the determined pore volume (V_p) except where indicated: $D_{\mathrm{H2}} = N_{\mathrm{H2}} / V_p$. [k] calculated from the absorbed H_2 values (N_{H2}) and V_{PLAT}; [l] Obtained by using equation of $D_{\mathrm{H2-V}} = N_{\mathrm{H2-max}} * D_{\mathrm{clcd}}$, where D_{clcd} has the same definition as above, and $N_{\mathrm{H2-max}}$ is the maximum adsorbed amount determined from Langmiur plots or the actual saturation value at high pressure (≥ 20 bar).

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