A bimetallic pillared-layer metal-organic coordination framework with a 3D biporous structure

Tapas Kumar Maji,* Suchetan Pal, K. L. Gurunatha, A. Govindaraj, C. N. R. Rao*

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore- 560 064, India. E-mail: tmaji@jncasr.ac.in

Experimental section

Synthesis of $\{[Mn_3(4,4'\text{-bipy})_3(H_2O)_4][Fe(CN)_6]_2.2(4,4'\text{-bipy}).3(H_2O)\}_n$ (1): An aqueous solution (12.5 mL) of $K_3Fe(CN)_6$ (0.25 mmol, 0.0426 g) was added to an ethanolic solution (12.5 mL) of 4,4′-bipyridyl (0.25 mmol, 0.039 g) and stirred for 30 min. $MnCl_2.4H_2O$ (0.25 mmol, 0.0494 g) was dissolved in 12.5 ml distilled water and 2.5 mL of this metal solution was carefully layered with the 2.5 mL of mixed 4,4′-bipyridyl and $K_3Fe(CN)_6$ solution using a ethanol : water buffer solution (1 mL) in a crystal tube. After 15 days brown square blocks were appeared in the middle of the tube and separated and washed with ethanol (Yield : ~ 60 %). The bulk amount of the sample was prepared by the direct mixing of the reagents in ethanol / water mixed solution with stirring for 24 h and the phase purity was checked with the PXRD. This powdered sample was used for characterization of different physical properties. IR: ν(C≡N) 2067 cm^{-1} and 2129 cm^{-1}; ν(C=C): 1610 cm^{-1}, 1540 cm^{-1}; ν(O-H): 3481 cm^{-1} and 3571 cm^{-1}. Anal. cald. for $C_{62}H_{54}Fe_2Mn_3N_{22}O_7$: C, 49.74; H, 3.61; N, 20.59. Found: C, 48.68; H, 3.31; N, 20.66%.

Physical Measurement: Powder XRD pattern of the products were recorded by using Cu-K_{α} radiation (Bruker D8 Discover; 40 kV, 30 Ma)). The pattern was agreed with those calculated from single crystal structure determination. Thermogravimetric analysis (TGA) was carried out (Metler Toledo) in nitrogen atmosphere (flow rate = 50 ml min^{-1}) in the temperature range 25 – 500 °C (heating rate = 2°C min^{-1}). Infra-red (IR) spectroscopic studies was carried out in the mid-IR region as KBr pellet (Bruker IFS-66v). Magnetic studies were performed on a 5 mg batch of crystalline sample using Vibrating Sample Magnetometer (VSM) in physical property measurement system (PPMS, Quantum Design, USA).

X-ray Single crystal Measurement: A brown color square block single crystal of the compound **1** was carefully selected under a polarizing microscope and fixed to a thin glass fiber by commercially available glue. X-ray single crystal structural data was collected by a Bruker Smart –CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source ($Mo_{K\alpha}$ radiation, 0.71073 Å) operating at 50 kV and 30 mA. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program. Some hydrogen atoms were geometrically placed, but most of them were located by the Fourier difference synthesis. The hydrogen atoms on the guest water molecules could not be located. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non hydrogen atoms, isotropic thermal parameters for the hydrogen atoms. All calculations were carried out using SHELXL-97, SHELXS-97, PLATON-99 and WinGX programme (Ver-1.64). The selected bond lengths and angles were given in **Table S2** and **Table S3**, respectively.

Adsorption Study: N_2 (77K), CO_2 (195K), and H_2 (77 K) adsorption-desorption isotherms were measured using QUANTACHROME AUTOSORB-1C analyzer. The adsorption of different solvents (like MeOH (293K), H_2O, EtOH, CH_3CN and C_6H_6 (298 K) were measured in the gaseous state by using BELSORP-aqua-3 analyzer. In all the measurements, in the sample tube adsorbent sample (~100 –150 mg) was placed and prepared at 473 K for about 5 hours under vacuum prior to measurement of the isotherms. The different solvent molecules used to generate the vapor were degassed fully by repeated evacuation. Helium gas at a certain pressure was introduced in the gas chamber and was allowed to diffuse into the sample chamber by opening a valve. The adsorbate was placed into the sample tube, then the change of the pressure was monitored and the degree of adsorption was determined by the decrease of the pressure at the equilibrium state. All operations were computer–controlled and automatic.

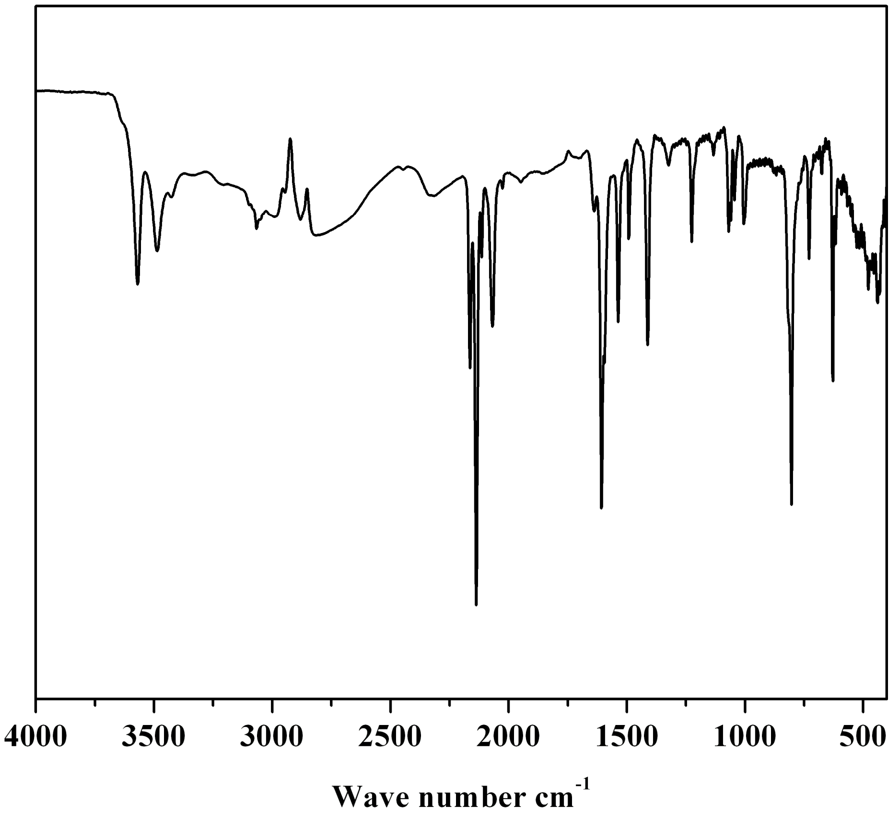

Fig. S1: IR spectra of $\{[Mn_3(4,4'\text{-bipy})_3(H_2O)_4][Fe(CN)_6]_2.2(4,4'\text{-bipy}).3(H_2O)\}_n$ **(1)**

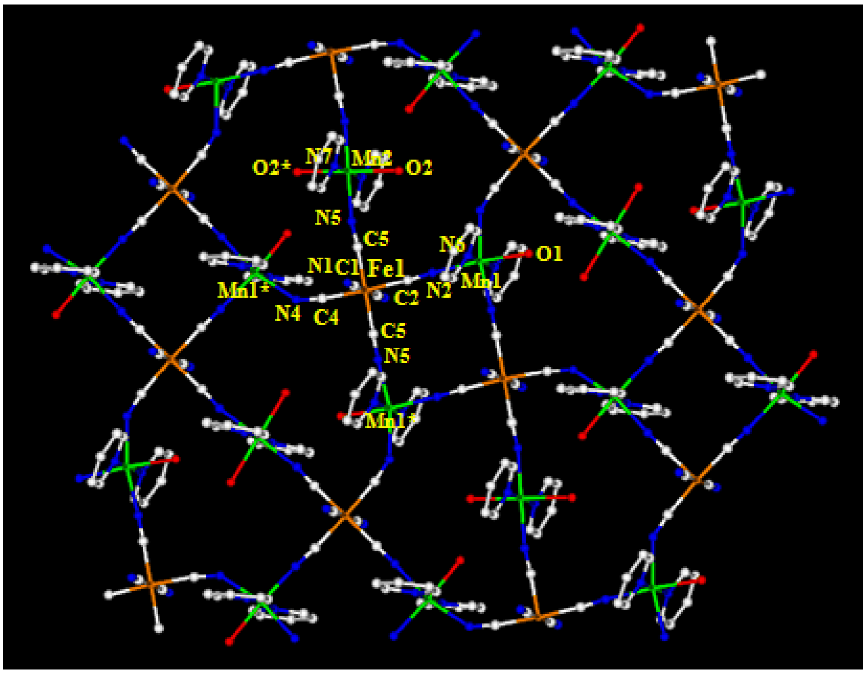

Fig. S2: View of the building unit showing the linking of Fe(CN)$_6^{3-}$ with Mn(II) in 2D layer which is connected by the 4,4′-bipy.

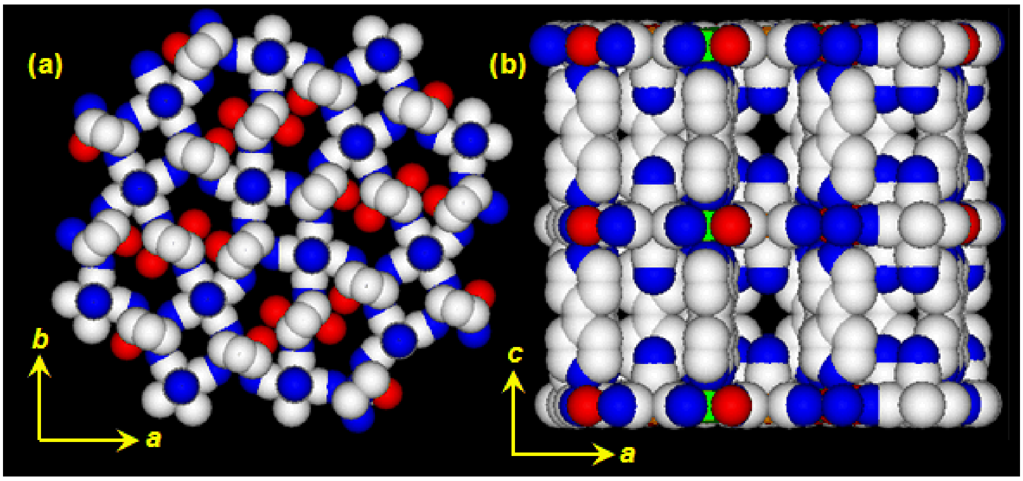

Fig. S3: Views of the 3D network of **1** along the crystallographic *c* and *b*-axis respectively.

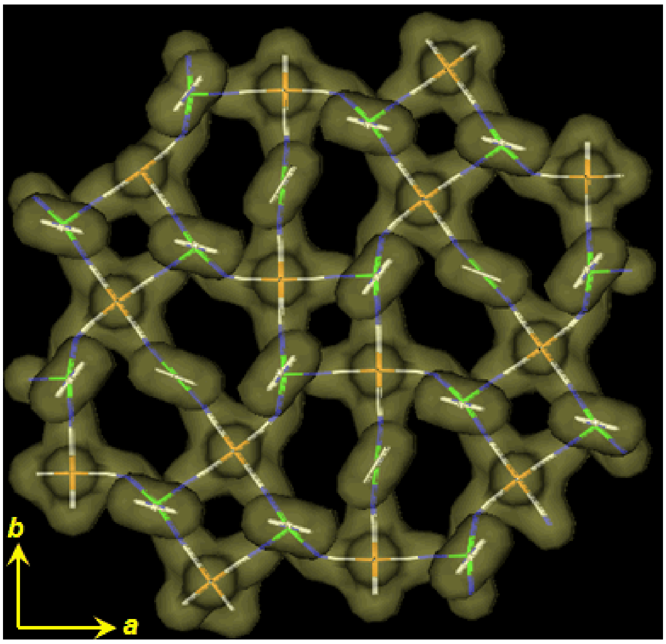

Fig. S4: View of the two different pore surfaces.

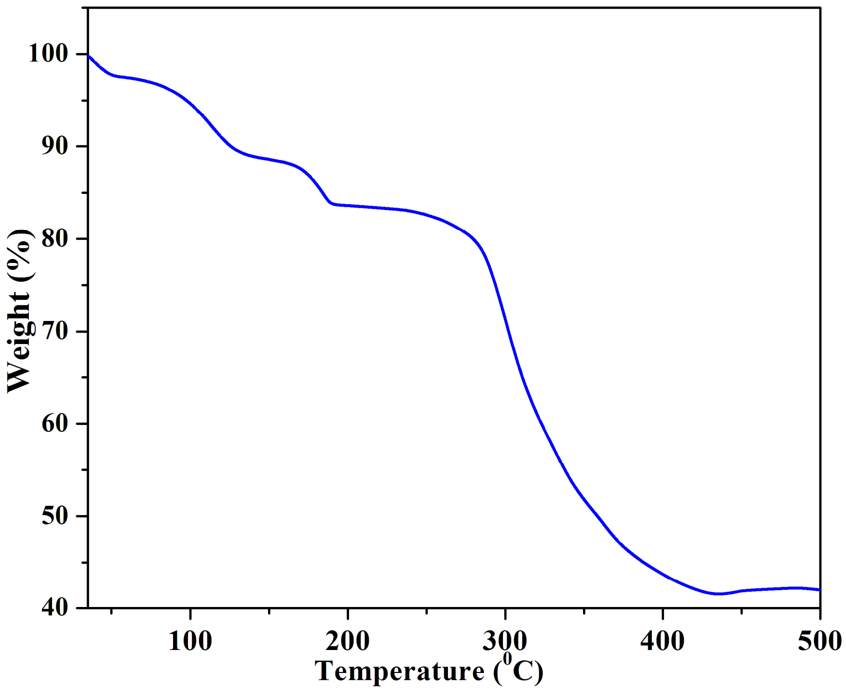

Fig. S5: TGA analysis of $\{[Mn_3(4,4'\text{-bipy})_3(H_2O)_4][Fe(CN)_6]_2.2(4,4'\text{-bipy}).3(H_2O)\}_n$ **(1)** over the temperature range from 25-500°C at heating rate of 2°C/min under the N_2 atmosphere.

Description of TGA: Thermogravimetric analysis (TGA) of freshly prepared powder sample of $\{[Mn_3(4,4'\text{-bipy})_3(H_2O)_4][Fe(CN)_6]_2.2(4,4'\text{-bipy}).3(H_2O)\}_n$ (**1**), shows stepwise release of the guest (H_2O & 4,4'-bipy) and coordinated water molecules. The first step (~30-60 °C) corresponds to the two guest water molecules (calc. 2.43 wt% and obs. 2.67 wt%) of the formula and the volatility of one water molecules (O4, high thermal parameters) of the crystallized solvents contributes the discrepancy in the first step of TGA result. The second step (~85-140°C) corresponds to the release of one 4,4'-bipy (calc. 10.53 wt% and obs. 9.67 wt%) and the third step (~ 170 - 190°C) suggests the removal of the four coordinated water molecules (calc. 4.86 wt % and obs. 5.21 wt. %). The solid with incomplete removal of 4,4'-bipy stable up to 285°C without further weight loss and upon further heating decomposes to unidentified product. Such phenomenon with incomplete removal of the guest molecules in porous frameworks was recently reported by Rosseinsky *et. al.*[1] For the sorption measurement we have degassed the assysnthesized sample at 473 K about five hours under high vacuum (10^{-1} pa). We have analysed the elemental analysis after pretreatment, which shows the composition of {[Mn₃(4,4'-

bipy)$_3$][Fe(CN)$_6$]$_2$}$_n$ (**1′**) suggesting removal of all guest H_2O and 4,4'-bipy and coordinated water molecules. Anal. cald. for $C_{42}H_{24}Fe_2Mn_3N_{18}$: C, 47.48; H, 2.26; N, 23.74. Found: C, 46.38; H, 3.02; N, 22.96%.

1) J. P. Barrio, J. –N. Rebilly, B. Carter, D. Bradshaw, J. Bacsa, A. Y. Ganin, H. Park, A. Trewin, R. Vaidhyanathan, A. I. Cooper, J. E. Warren, and M. J. Rosseinsky, *Chem. Eur. J.*, 2008, **14**, 4521

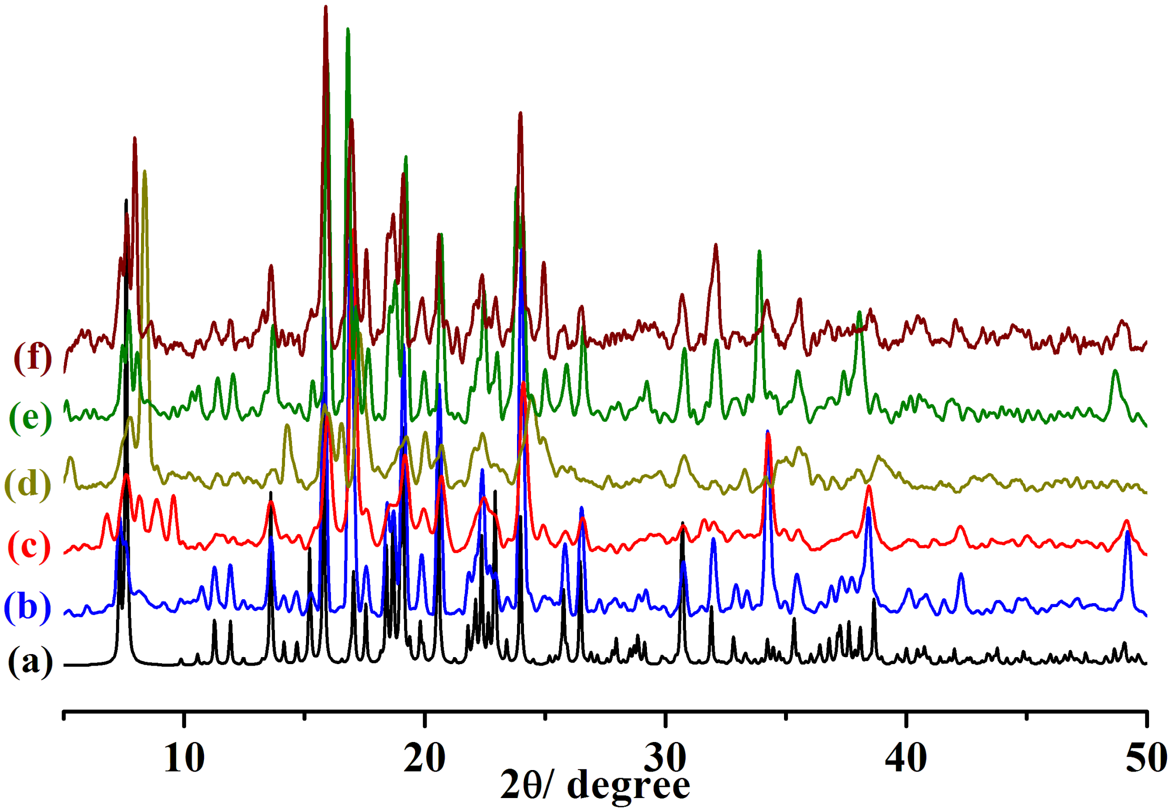

Fig. S6: XRPD patterns of {[Mn_3(4,4'-bipy)$_3$(H_2O)$_4$][Fe(CN)$_6$]$_2$.2(4,4'-bipy).3(H_2O)}$_n$ (**1**) at different states. (a) Simulated; (b) as-synthesized; (c) at 190°C under vacuum; (d) exposed to the water vapor; (e) exposed to MeOH vapor and (f) exposed with EtOH vapor.

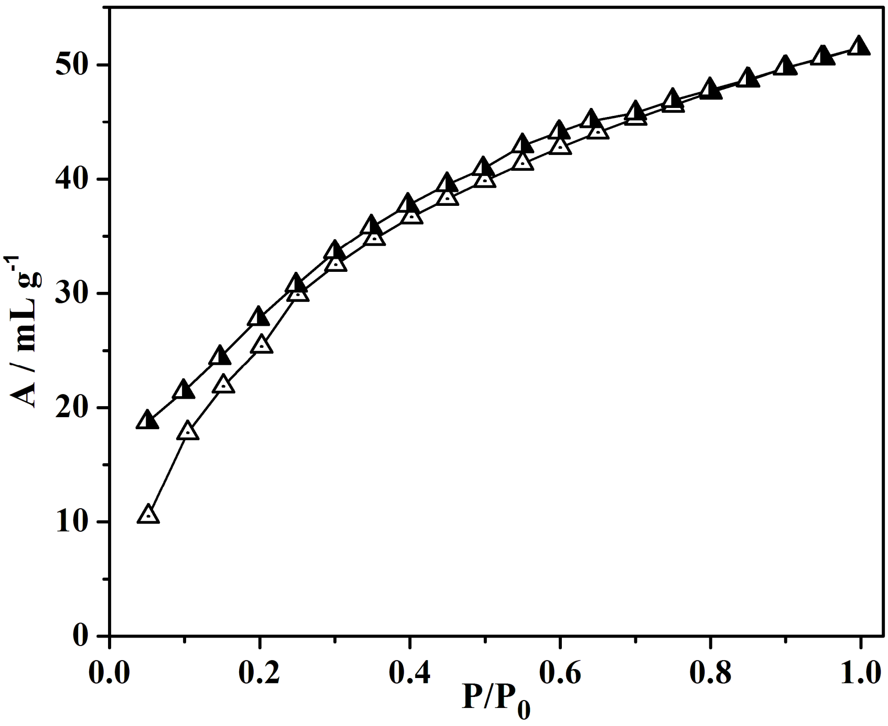

Fig. S7; Adsorption isotherm of H_2 at 77 K for **1**

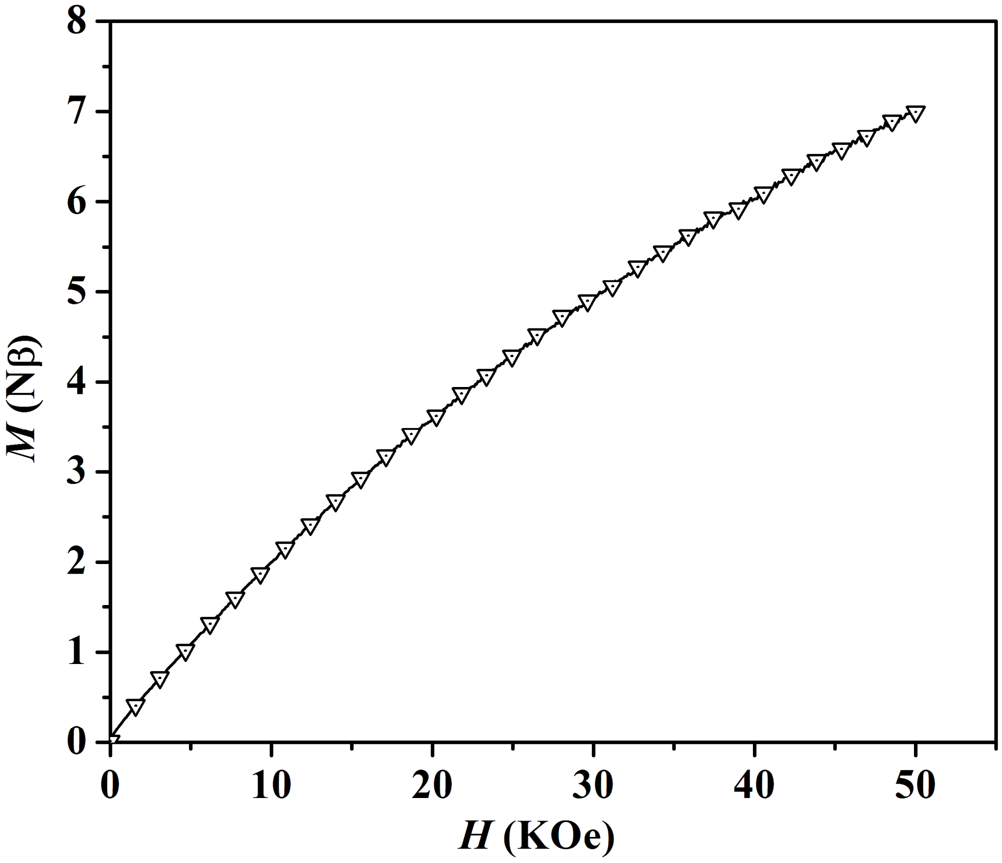

Fig. S8: Magnetization of **1** at 2.5 K up to 5 T.

Table S1: Hydrogen uptake of porous coordination framework (surface area ≤ 1000 m^2/g) at 77 K and 1 atm.

Compounds	**Surface Area ($m^2\,g^{-1}$)**	**H_2 uptake (wt %)**	**Conditions**	**Ref.**
$[Pd(4\text{-}pymo)_2]_n$	65	0.03	77 K, 900 Torr	[1]
$[Zn(ADC)(4,4'\text{-}bpe)_{0.5}]_n$	100	0.62	77 K, 1 atm	[2]
$[Co(2,6\text{-}NDC)(4,4'\text{-}bpy)_{0.5}]_n$	115	0.72	77 K, 1 atm	[3]
$[Zn_4O(H_2O)_3(adc)_3]_n$	150	0.4	77 K, 1atm	[4]
This compound	150	0.53	77 K, 1 atm	This work
$[Mg_3(2,6\text{-}NDC)_3]_n$	190	0.46	77 K, 880 Torr	[5]
$H_2[Ni_3O(H_2O)_3(TATB)_2]_n$	225	0.63	77 K, 760 Torr	[6]
$[Mn(HCO_2)_2]_n$	240	0.9	78 K, 1 atm	[7]
$[Mn_3(BDT)_3]_n$	290	0.97	77 K, 880 Torr	[8]
$[Zn_2(CNC)_2(DPT)]_n$	342	1.28	77 K, 1 atm	[9]
$[Cu(2\text{-}pymo)_2]_n$	350	0.86	77 K, 900 Torr	[1]
$[Co_3(BDC)_3(dabco)]_n$	360	1.00	77 K, 0.93 bar	[10]
$[Zn_3(NTB)_2(EtOH)_2]_n$	419	1.0	77 K, 1 atm	[11]
$[Cu_2(TCPPDA)(H_2O)_2]_n$	627	1.4	77 K, 1 atm	[12]
$[Co_3(2,4\text{-}pdc)_2(\mu_3\text{-}OH)_2]_n$	630	1.6	77 K, 760 Torr	[13]
$[Co_2(6\text{-}mna)_2]_n$	420	0.67	77 K, 760 Torr	[13]
$[Mn_2(BDT)Cl_2]_n$	530	0.82	77 K, 880 Torr	[8]
$Fe_4[Fe(CN)_6]_3$	550	1.2	77 K, 890 Torr	[14]
$Ni_3[Co(CN)_6]_2$	560	1.4	77 K, 890 Torr	[15]
$Ga[Co(CN)_6]$	570	1.1	77 K, 890 Torr	[14]
$[Pd(2\text{-}pymo)_2]_n$	600	1.29	77 K, 900 Torr	[1]
$[Co_3(2,4\text{-}pdc)_2(\mu_3\text{-}OH)_2]_n$	630	1.6	77 K, 760 Torr	[13]
$[Fe_3O(F_4BDC)_3(H_2O)_3]_n$	635	0.9	77 K, 1 bar	[16]
$[Zn_3(BDT)_3]_n$	640	1.46	77 K, 880 Torr	[8]
$Zn_3[Co(CN)_6]_2$	720	1.4	77 K, 890 Torr	[15]
$[Cu_2(L_3)(H_2O)_2]_n$	733	0.8	77 K, ~1atm	[17]
$Cu_3[Co(CN)_6]_2$	750	1.8	77 K, 890 Torr	[14]
$[Zn_2(2,6\text{-}NDC)_2(diPyNI)]_n$.-**$Li^+$**	756	1.63	77 K, 1 atm	[18]
$Fe_3[Co(CN)_6]_2$	770	1.4	77 K, 890 Torr	[15]
$[Zn_3(bpdc)_3(4,4'\text{-}bpy)]_n$	792	1.74	77 K, 1 atm	[19]
$Zn(Pur)_2$	800	1.1	77 K, ~800 Torr	[20]
$Co_3[Co(CN)_6]_2$	800	1.5	77 K, 890 Torr	[15]
$[Zn_2(2,6\text{-}NDC)_2(diPyNI)]_n$.	802	0.93	77 K, 1 atm	[11]
$[Ni(cyclam)(bpydc)]_n$	817	1.1	77 K, 1 atm	[21]
$Mn_3[Co(CN)_6]_2$	870	1.6	77 K, 890 Torr	[15]
$[Zn_2(tmBDC)_2(dabco)]_n$	920	1.8	78 K, 1 atm	[22]

[Co$_3$(bpdc)$_3$(4,4'-bpy)]$_n$	922	1.98	77 K, 1 atm	[19]
[Zn$_2$(BDC)$_2$(4,4'-bpy)]$_n$	946	0.8	77 K, 1 atm	[23]
[Zn$_2$(1,4-NDC)$_2$(dabco)]$_n$	1000	1.7	78 K, 1 atm	[22]

References:
[1] J. A. R. Navarro, E. Barea, J. M. Salas, N. Masciocchi, S. Galli, A. Sironi, C. O. Ania and J. L. B. Parra, *Inorg. Chem.,* 2006, **45**, 2397.
[2] B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky and H.-C. Zhou, *Inorg. Chem.,* 2007, **46,** 8490.
[3] B. Chen, S. Ma, E. J. Hurtado, E. B. Lobkovsky, C. Liang, H. Zhu and S. Dai, *Inorg. Chem.,* 2007, **46**, 8705.
[4] S. Ma, X.-S. Wang, C. D. Collier, E. S. Manis and H.-C. Zhou, *Inorg. Chem.,* 2007, **46**, 8499.
[5] M. Dincă and J. R. Long, *J. Am. Chem. Soc.,* 2005, **127**, 9376.
[6] S. Ma, X.-S. Wang, E. S. Manis, C. D. Collier and H.-C. Zhou, *Inorg. Chem.,* 2007, **46**, 3432.
[7] D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, *J. Am. Chem. Soc.,* 2004, **126**, 32.
[8] M. Dincă, A. F. Yu and J. R. Long, *J. Am. Chem. Soc.,* 2006, **128**, 8904.
[9] M. Xue, S. Ma, Z. Jin, R. M. Schaffino, G.-S. Zhu, E. B. Lobkovsky, S.-L. Qiu and B. Chen, *Inorg. Chem.,* 2008, **47**, 6825.
[10] H. Chun, H. Jung, G. Koo, H. Jeong and D.-K. Kim, *Inorg. Chem.,* 2008, **47**, 5355.
[11] M. P. Suh, Y. E. Cheon and E. Y. Lee, *Chem. Eur. J.,* 2007, **13**, 4208.
[12] D. Sun, Y. Ke, T. M. Mattox, B. A. Ooro and H.-C. Zhou, *Chem. Commun.,* 2005, 5447.
[13] S. M. Humphrey, J.-S. Chang, S. H. Jhung, J. W. Yoon and P. T. Wood, *Angew. Chem., Int. Ed.,* 2007, **46**, 272.
[14] S. S. Kaye and J. R. Long, *Catalysis Today,* 2007, **120**, 311.
[15] S. S. Kaye and J. R. Long, *J. Am. Chem. Soc.,* 2005, **127**, 6506.
[16] J. H. Yoon, S. B. Choi, Y. J. Oh, M. J. Seo, Y. H. Jhon, T.-B. Lee, D. Kim, S. H. Choi and J. Kim, *Catalysis Today* ,2007, **120**, 324.
[17] L. Ma, J. Y. Lee, J. Li and W. Lin, *Inorg. Chem.,* 2008, **47**, 3955.
[18] K. L. Mulfort, J. T. Hupp, *J. Am. Chem. Soc.,* 2007, **129**, 9604.
[19] J. Y. Lee, L. Pan, S. P. Kelly, J. Jagiello, T. J. Emge and J. Li, *Adv. Mater.,* 2005, **17**, 2703.
[20] H. Hayashi, A. P. Côte, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature Mater.,* 2007, **6**, 501.
[21] E. Y. Lee and M. P. Suh, *Angew. Chem., Int. Ed.,* 2004, **43**, 2798.
[22] H. Chun, D. N. Dybtsev, H. Kim and K. Kim, *Chem. Eur. J.,* 2005, **11**, 3521.
[23] B. Chen, C. Liang, J. Yang, D. S. Contreras, Y. L. Clancy, E. B. Lobkovsky and O. M. Yaghi, S. Dai, *Angew. Chem., Int. Ed.,* 2006, **45**, 1390.

Table S2: Bond Distances (Å) for {[Mn_3(4,4'-bipy)$_3$(H_2O)$_4$][Fe(CN)$_6$]$_2$.2(4,4'-bipy).3(H_2O)}$_n$ (**1**)

Fe1-C1	1.965(5)
Fe1-C2	1.928(5)
Fe1-C3	1.927(5)
Fe1-C4	1.946(5)
Fe1-C5	1.926(5)
Fe1-C1_i	1.965(5)
Mn1-O1	2.200(4)
Mn1-N2	2.158(5)
Mn1-N6	2.269(3)
Mn1-N5_b	2.182(5)
Mn1-N6_i	2.269(3)
Mn2-O2	2.263(3)
Mn2-N3	2.178(5)
Mn2-N7	2.265(5)
Mn2-O2_a	2.263(3)
Mn2-N3_a	2.178(5)
Mn2-N7_f	2.265(5)

Symmetry code: a = 1-x,-y,z; b = 2-x,-y, z; g = 2-x,-y,1-z; i = x, y,1-z.

Table S3: Bond Angles (º) for{[Mn_3(4,4'-bipy)$_3$(H_2O)$_4$][Fe(CN)$_6$]$_2$.2(4,4'-bipy).3(H_2O)}$_n$ (**1**).

C1-Fe1-C2	89.33(11)
C1-Fe1-C3	90.10(10)
C1-Fe1-C4	90.67(11)
C1-Fe1-C5	89.90(10)
C1-Fe1-C1_i	178.65(15)
C2-Fe1-C3	88.5(2)
C2 -Fe1-C4	176.7(2)
C2-Fe1-C5	91.4(2)

C1_i -Fe1-C2	89.33(11)
C3 -Fe1-C4	88.2(2)
C3-Fe1-C5	179.89(12)
C1_i-Fe1-C3	90.10(10)
C4-Fe1-C5	92.0(2)
C1_i-Fe1-C4	90.67(11)
C1_i -Fe1-C5	89.90(10)
O1-Mn1-N2	175.78(16)
O1-Mn1-N6	88.13(8)
O1-Mn1-N5_b	83.45(17)
O1-Mn1-N6_i	88.13(8)
N2 -Mn1-N6	91.84(8)
N2-Mn1-N5_b	92.34(19)
N2 -Mn1-N6_i	91.84(8)
N5_b-Mn1-N6	89.40(8)
N6 -Mn1 -N6_i	176.17(12)
N5_b-Mn1-N6_i	89.40(8)
O2 -Mn2-N3	94.92(13)
O2-Mn2-N7	90
O2 -Mn2-O2_a	180
O2-Mn2-N3_a	85.08(13)
O2-Mn2 -N7_f	90
N3-Mn2-N7	90
O2_a-Mn2-N3	85.08 (13)
N3-Mn2 -N3_a	180
N3-Mn2-N7_f	90
O2_a-Mn2-N7	90
N3_a-Mn2-N7	90
N7 -Mn2-N7_f	180
O2_a -Mn2-N3_a	94.92(13)
O2_a-Mn2-N7_f	90
N3_a-Mn2 -N7_f	90

Symmetry code a = 1-x,-y,z; b = 2-x,-y, z; g = 2-x,-y,1-z; i = x, y,1-z.