Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

for

Room temperature synthesis of Fe(II) based porous MOF with multiple open metal sites for high gas adsorption property

Sushil Kumar*[a], Aayushi Arora[a], Jolly Kaushal,[a] Preeti Oswal,[a] Arun Kumar [a] and Kapil Tomar[b]

[a] *Department of Chemistry, School of Physical Sciences (SoPS), Doon University, Dehradun, Dehradun-248001, Uttarakhand, India. Email: sushilvashisth@gmail.com*

[b] *Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh India.*

EXPERIMENTAL SECTION

Materials

The metal salt and other reagent-grade chemicals were procured from Sigma-Aldrich and used as received. All solvents were procured from S. D. Fine Chemicals, India. These solvents were purified following standard methods prior to use.

Physical measurements

Thermogravimetric analyses (TGA) were acquired on a Mettler Toledo Star system (heating rate of 5 °C/min). Microanalyses of **1** were carried out by using a CE-440 elemental analyzer (Exeter Analytical Inc.). Powder X-ray diffraction spectra (Cu K_α radiation, scan rate 3°/min, 293 K) were obtained on a Bruker D8 Advance series 2 powder X-ray diffractometer. Gas adsorption measurements were performed on Quantachrome Quadrasorb automatic volumetric instrument.

X-ray structural studies

Suitable single crystal of **1** was mounted on a Bruker SMART II diffractometer equipped with a graphite monochromator and Mo–Kα (λ = 0.71073 Å, 140 K) radiation. Data collection was performed using φ and ω scan. The structure was solved using direct method followed by full matrix least square refinements against F^2 (all data HKLF 4 format) using SHELXL 2014/7 program package. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non-hydrogen atoms. Determinations of the crystal system, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and multi–scan absorption correction were applied. Non–hydrogen atoms were refined with hydrogen atoms were placed geometrically and refined using the riding model. The crystal and refinement data are collected in Table S1 while selected bond distances and angles are given in Table S3.

Experimental procedure for compounds

Bipyrazole (BPz) was prepared according to the reported procedure [S1].

Preparation of MOF, $[NH_4][Fe_2(OH)(BTtC)(BPz)_{0.5}(H_2O)(DMF)].DMF.4H_2O$ (1)

Mohr's salt, $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ (0.4 mmol) was taken in 20 mL of water and stirred for 10 min to dissolve completely. BTtC and BPz (0.2 mmol each) were dissolved in 2 mL of methanol, and 2 mL of this solution was slowly and carefully layered with 2 mL of the above aqueous solution, using 1 mL of DMF as a third middle layer to slow down the diffusion, in a narrow glass tube. Cube-shaped light brown crystals were formed within two weeks in the tube. The crystals were separated, washed with cold water and acetone, and air-dried (yield 43%). Anal. Calcd for $C_{21}H_{38}Fe_2N_5O_{16}$: C, 34.63; H, 5.26; N, 9.62%. Found: C, 34.27; H 5.04; N, 9.45%. FT-IR (KBr pellet, 4000–400 cm^{-1}): 3396, 3149, 3048, 1611, 1538, 1400, 1311, 1259, 1103, 1047, 1015, 870, 818, 735, 675, 575 and 484.

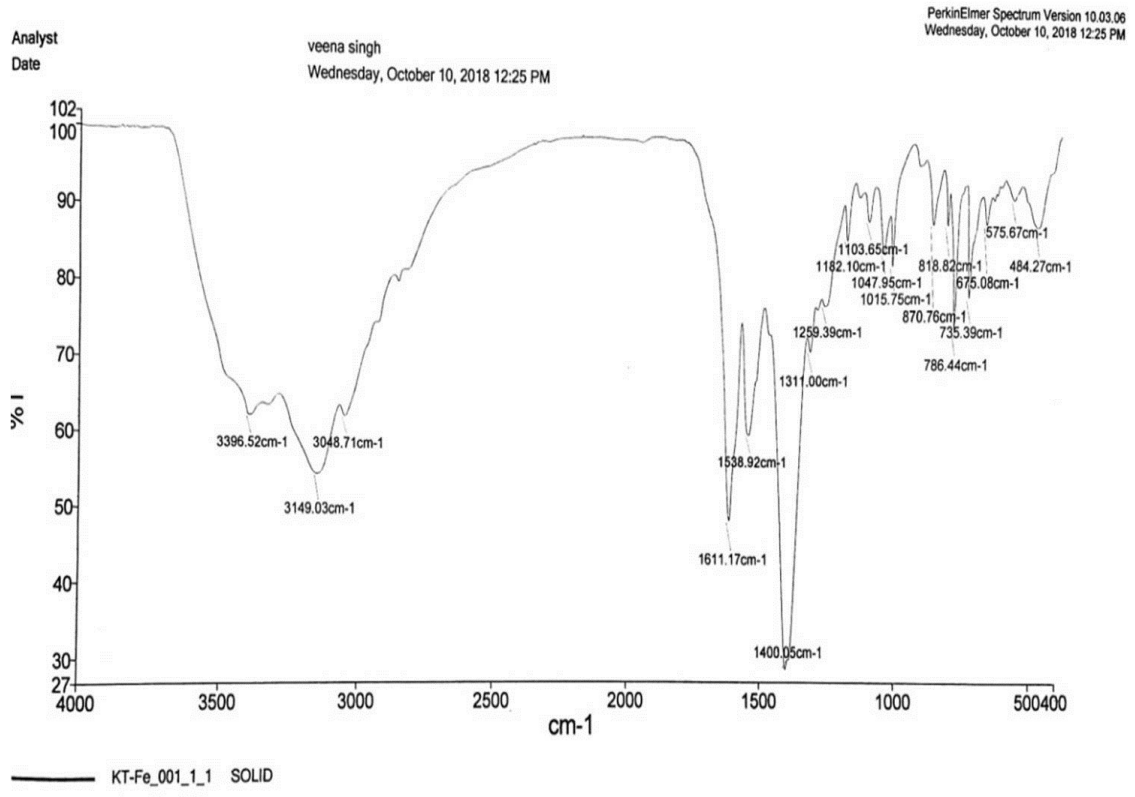

Fig. S1 IR spectrum of **1**.

Table S1. X-ray crystallographic data and refinement parameters for **1**.

MOF **1**	
Formula	$C_{18}H_{19}Fe_2N_3O_{11}$
M_w (g mol^{-1})	565.05
Crystal system	monoclinic
Space group	*C*2/c
a (Å)	29.03(2)
b (Å)	18.120(11)
c (Å)	14.06(1)
α (°)	90
β (°)	113.699(14)
γ (°)	90
V (Å^3)	6772(8)
Z	8
ρ_{calcd} (g cm^{-3})	1.109
μ(MoKα) (mm^{-1})	0.900
F(000)	2304.0
Goodness-of-fit	0.970
R1, wR2 (I > 2σI)	0.0694, 0.1820
R1, wR2 (all data)	0.1096, 0.2112
CCDC Number	1874397

R1=Σ||Fo|-|Fc||/Σ|Fo| & wR2=|Σw(|Fo|2- |Fc|2)|/Σ|w(Fo)2|1/2.

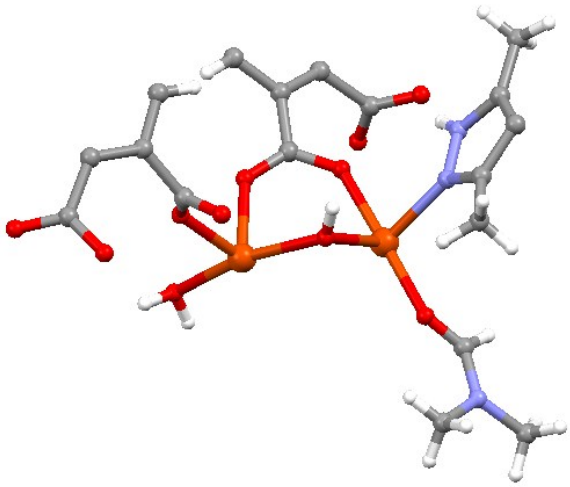

Fig. S2 Asymmetric unit of **1**.

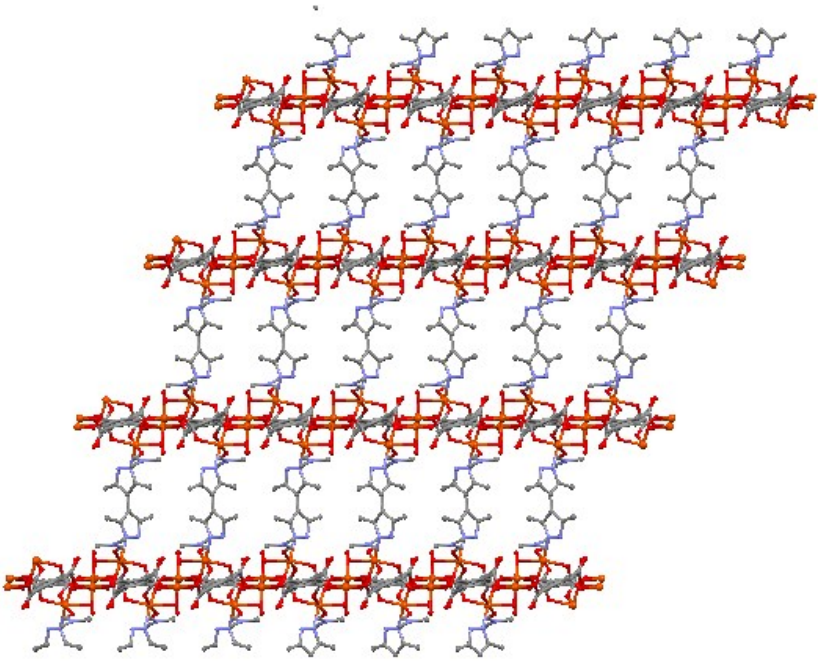

Fig. S3 A view of the 2D sheet structure of **1**.

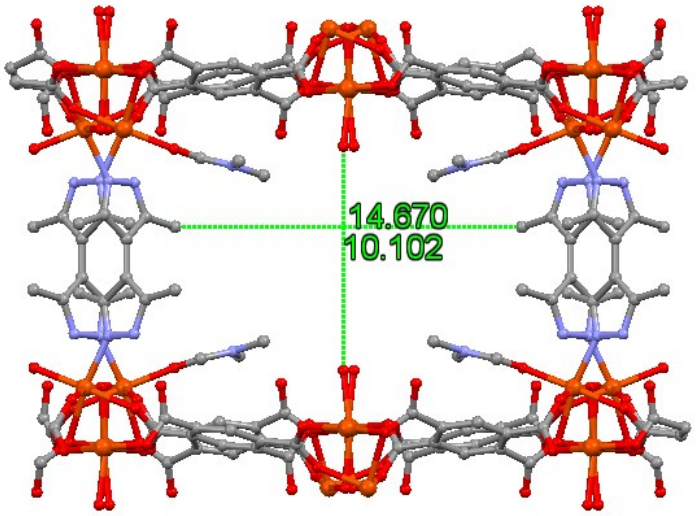

Fig. S4 A view of the cavity size in **1**.

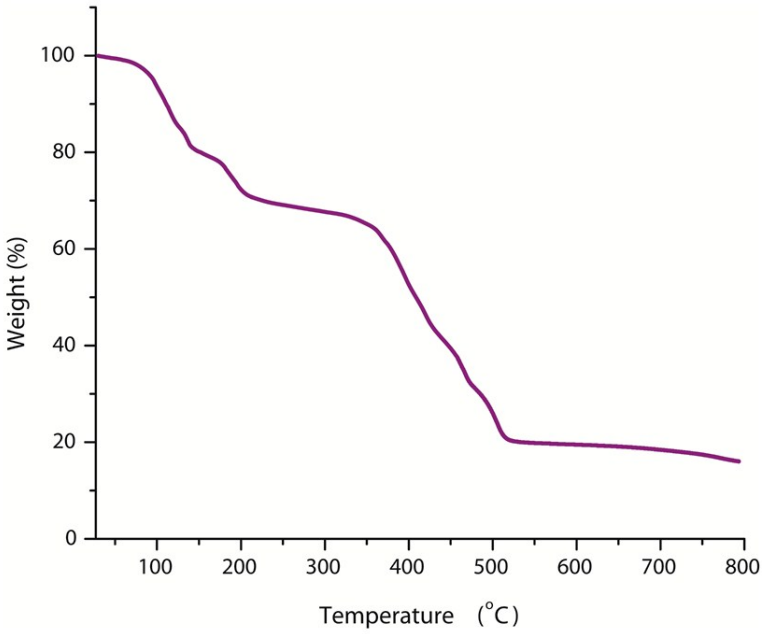

Fig. S5 Thermo gravimetric analysis (TGA) curve of **1**.

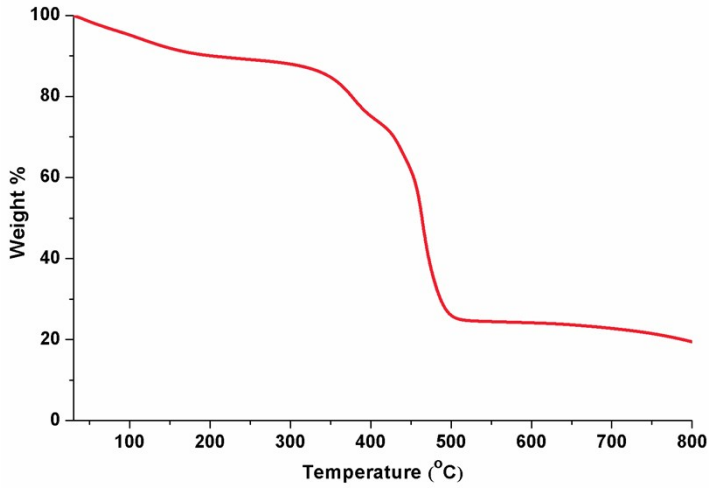

Fig. S6 Thermo gravimetric analysis (TGA) curve of activated **1**.

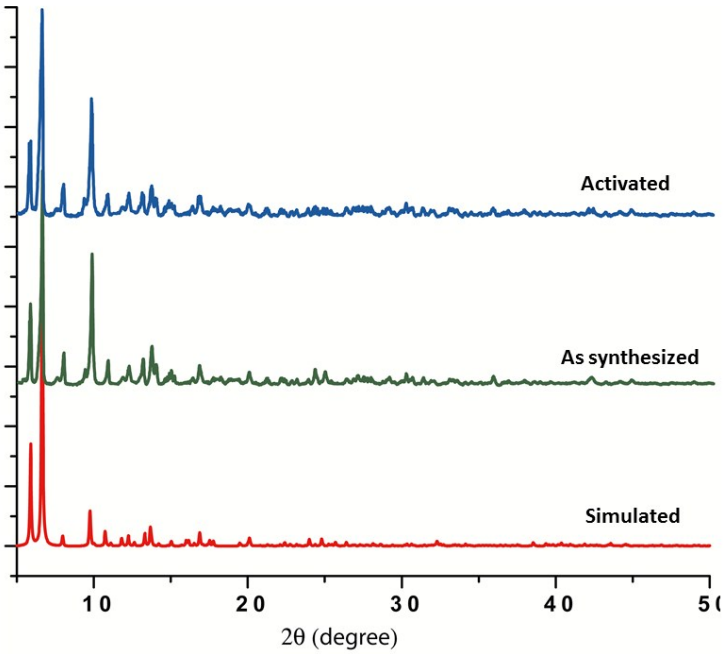

Fig. S7 PXRD patterns of the simulated (red), as synthesized, (green), and after activation (blue) for **1**.

Table S2: Indexing result from the powder data of as-synthesized compound MOF **1**

	Peak positions			
	2theta	d	FWHM	100.*I/Imax
1)	5.8996	14.968209	0.0943	33.67
2)	6.6407	13.299402	0.0947	100.00
3)	7.9793	11.071009	0.0967	3.30
4)	9.7589	9.055739	0.0938	11.60
5)	10.7403	8.230392	0.0977	4.90
6)	11.1012	7.963622	0.0971	0.79
7)	11.8187	7.481735	0.0928	2.45

8)	12.2419	7.224046	0.0932	3.37
9)	12.6384	6.998237	0.0944	1.07
10)	13.3186	6.642359	0.1018	3.93
11)	13.6811	6.467155	0.1011	6.15
12)	14.2202	6.223150	0.0848	0.69
13)	15.0396	5.885900	0.0923	1.54
14)	16.0004	5.534564	0.0916	1.13
15)	16.1594	5.480460	0.0908	1.78
16)	16.5380	5.355826	0.0865	0.69
17)	16.8810	5.247758	0.0872	4.26
18)	17.5204	5.057675	0.0986	1.58
19)	17.7612	4.989637	0.0984	1.38
20)	19.4810	4.552867	0.1091	0.94
21)	20.1009	4.413825	0.1267	2.62
22)	22.4000	3.965719	0.1395	1.09
23)	24.0000	3.704837	0.0770	2.21
24)	24.8008	3.587002	0.0969	2.30

Dicvol06 (cpu time): 0h 0m 0.031s

Dicvol06 (elapsed time): 0h 0m 5.848s

List of plausible cell parameters:

---

n.	prog	a	b	c	alpha	beta	gamma	vol	M20	FomNew	McM20	NIX	sym
1	D	26.7036	18.1265	14.0625	90.00	95.15	90.00	6779.33	17.80	-	-	0	Mono
2	D	29.0414	18.1265	14.0625	90.00	113.68	90.00	6779.33	17.80	-	-	0	Mono

The following cell has been selected:

a= 29.041(11) b= 18.126(7) c= 14.062(5)

beta= 113.68(3) Volume= 6779(4)

Unit cell contents and scattering factor constants

Atom	Symbol	Number in cell	Atomic number
Hydrogen	H	19	1
Carbon	C	18	6
Nitrogen	N	3	7
Oxygen	O	11	8
Iron	Fe	2	26

f = sum (a(i) * exp(-b(i)*s2)) i=1,4 + c

	a(1)	b(1)	a(2)	b(2)	a(3)	b(3)	a(4)	b(4)	c
H	0.490	20.659	0.262	7.740	0.197	49.552	0.050	2.202	0.001
C	2.310	20.844	1.020	10.207	1.589	0.569	0.865	51.651	0.216
N	12.213	0.006	3.132	9.893	2.013	28.997	1.166	0.583	-11.529
O	3.048	13.277	2.287	5.701	1.546	0.324	0.867	32.909	0.251
Fe	11.769	4.761	7.357	0.307	3.522	15.354	2.304	76.880	1.037

Wave Length = 1.5406

***** Space Group Determination Section *****

++++ analysis by using the point group ++++

Laue group no. 1 P 1 2/m 1

Space Group Number: 10

Table Setting Choice: b

Crystal System: Monoclinic

Hall Symbol: -P 2y

Hermann-Mauguin Symbol: P 1 2/m 1

Laue Group Symbol: 2/m

Point Group Symbol: 2/m

Schoenflies Notation: C2h^1

Patterson Space Group: P2/m

Extinction Symbol: P 1 - 1

Centrosymmetry: Centric (-1 at origin)

Asymmetric Unit: 0<=x<=1/2; 0<=y<=1/2; 0<=z<1

Cheshire Cell: 0<=x<=1/2; 0<=y<=1/2; 0<=z<=1/2

Bravais Lattice: P

Lattice Symbol: mP

Multiplicity: 4

Frequency(no. in CSD): 110(0.01%), rank:111

List of centering operators: (0,0,0)+

List of all symmetry operators:

1) x, y, z 2) -x, y, -z

3) -x, -y, -z 4) x, -y, z

Number of Alternate origins is: 8

Origins: (0,0,0) (0,0,1/2) (0,1/2,0) (0,1/2,1/2) (1/2,0,0) (1/2,0,1/2) (1/2,1/2,0) (1/2,1/2,1/2)

Seminvariant condition : g g g

* Generated reflections information *

* *

* rho min = 0.00080 *

* rho max = 0.07526 *

* d (resolution) = 1.82264 *

* reflections nr. = 1269 *

* h k l (max) = 15 9 7 *

****

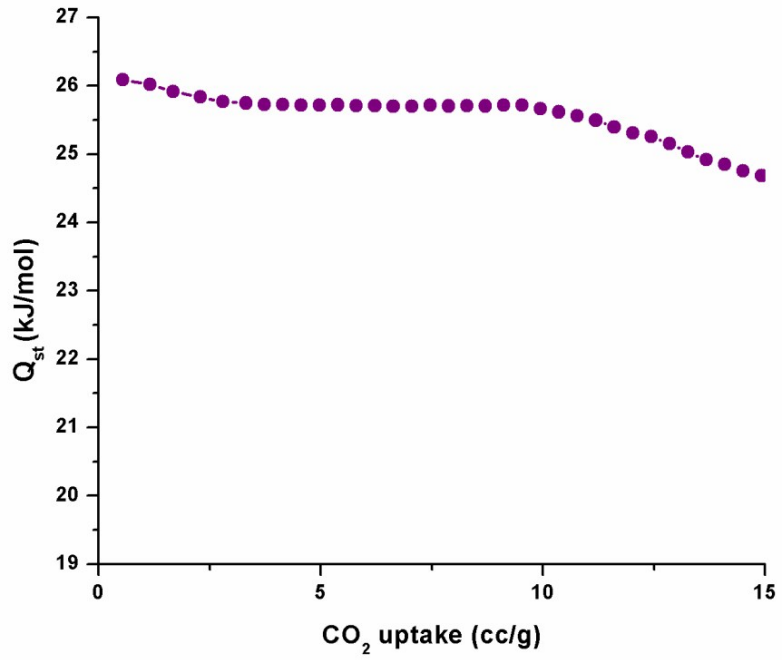

Fig. S8 Isosteric heat of adsorption (Q_{st}) for CO_2 gas.

Table S3 Bond parameters for **1**.

Bond distance (Å)			
Fe1—O2	2.087(6)	Fe2—O1	2.077(5)
Fe1—O3	2.217(5)	Fe2—O3	2.241(11)
Fe1—O4	2.097(9)	Fe2—O5	2.145(14)
Fe1—O6	2.211(6)	Fe2—O6	2.211(5)
Fe1—N1	2.162(8)	Fe2—O7	2.089(4)
Fe1—O9	2.078(6)	Fe2—O10	2.088(5)

Bond angle (°)			
O2—Fe1—O3	88.65(15)	O1—Fe2—O3	91.84(18)
O2—Fe1—O4	85.41(15)	O1—Fe2—O5	92.88(19)
O2—Fe1—O6	88.14(16)	O1—Fe2—O6	91.16(16)
O2—Fe1—N1	84.91(19)	O1—Fe2—O7	178.18(16)
O4—Fe1—O3	167.91(18)	O1—Fe2—O10	84.44(16)
O4—Fe1—O6	91.14(18)	O5—Fe2—O3	166.57(19)
O4—Fe1—N1	94.86(22)	O5—Fe2—O6	89.73(17)
O6—Fe1—O3	78.13(17)	O6—Fe2—O3	77.61(16)
N1—Fe1—O3	95.09(21)	O7—Fe2—O3	87.26(17)
N1—Fe1—O6	170.42(21)	O7—Fe2—O5	88.34(17)
O9—Fe1—O2	178.70(16)	O7—Fe2—O6	90.20(15)
O9—Fe1—O3	90.37(17)	O7—Fe2—O10	94.18(16)
O9—Fe1—O4	95.40(18)	O10—Fe2—O3	101.12(19)
O9—Fe1—O6	90.82(18)	O10—Fe2—O5	91.84(19)
O9—Fe1—N1	96.03(20)	O10—Fe2—O6	175.39(16)

Reference:

S1. Ponomarova, V. V.; Komarchuk, V. V.; Boldog, I.; Chernega, A. N.; Sieler, J.; Domasevitch, K. V. *Chem. Commun.* 2002, 436.