Electronic Supplementary Material (ESI) for Chemical Communications

Template Induced Structural Isomerism and Enhancement of Porosity in Manganese (II) based Metal Organic Frameworks (Mn-MOFs)

(Supporting Information: 38 pages including this page)

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Section S1: Detailed synthesis procedures for Mn-MOFs including multi-gram scale synthesis, experimental and simulated PXRD patterns

All reagents and solvents for synthesis and analysis were commercially available and used as received. The Fourier transform (FT) IR spectra (KBr pellet) were taken on a *PERKIN ELMER FT-IR SPECTRUM* (Nicolet) spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a Phillips PANAlytical diffractometer for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 2° min^{-1} and a step size of 0.02° in 2θ. Thermo-gravimetric experiments (TGA) were carried out in the temperature range of 25–800 °C on a SDT Q600 TG-DTA analyzer under N_2 atmosphere at a heating rate of 10 °C min^{-1}.

Thionyl chloride, hydrazine hydrate, diethyl ether, benzene, and *N*, *N*-dimethylformamide (DMF), benzene were purchased from Rankem chemicals. 5-amino isopthalic acid was purchased from the Aldrich Chemicals. All starting materials were used without further purification. All experimental operations were performed in air.

Synthesis of N,N-Dimethylformamide Azine Dihydrochloride (DMAz): 28.6 mL, 0.4 mol of Thionyl chloride ($SOCl_2$) was added with stirring to DMF (150 mL) at 5 ^{0}C. After addition keep this mixture at 5 ^{0}C for 24h and then added slowly aqueous hydrazine hydrate (5 mL, 0.1 mol) in 20 ml DMF. After addition the mixture was stirred at room temperature for 48h and the white precipitate of *N*, *N*-dimethylformamide azine dihydrochloride was collected by filtration and washed with DMF and diethyl ether: 19.1 gm; mp 251^{0}C.

FTIR: **(KBr 4000-400cm^{-1}):** 3473(s), 3223 (w), 2951(w), 2848(w), 2031(m), 1715(s), 1609(m), 1507(s), 1398(w), 1287(s), 1228(m), 1137(s), 1054(s), 1019(m), 877(m), 672(s), 654(m), 530(m), 496(m).

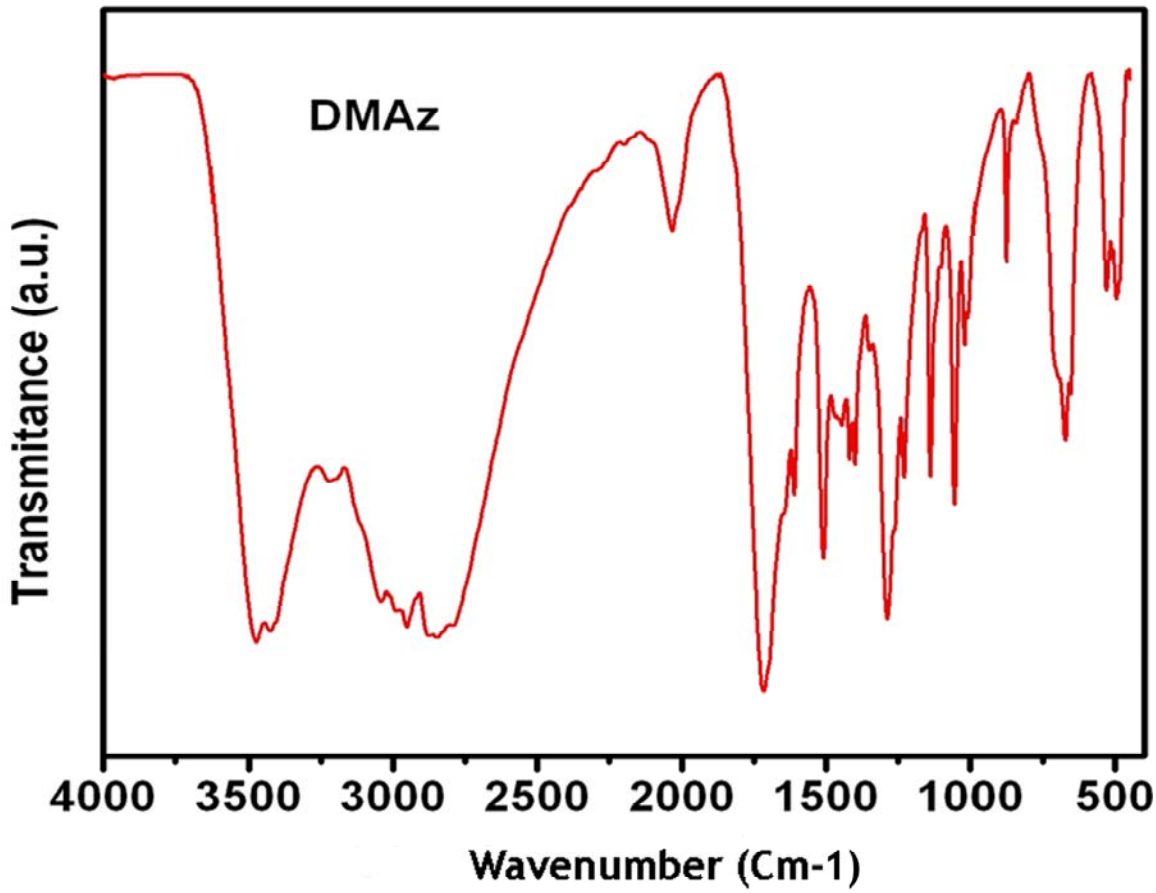

Figure S1. IR data of N,N-dimethylformamide azine dihydrochloride (DMAz).

Synthesis of 5-Triazole Isopthalic Acid : Refluxing a mixture of *N*, *N*-dimethylformamide azine dihydrochloride (4.0 g, 1.866 mmol) and 5-amino isopthalic acid (3.38 g, 1.866 mmol) in 50 ml benzene (Benzene is *carcinogenic*; reaction should be conducted in a fume hood) for 8h gave whitish solid. The solid was filtered and washed with ethanol (2 × 15 ml) and Diethyl ether (1 × 17 ml); yield: 2.38 g (68%);

Mn(5-TIA)(DMF) [Mn-5TIA-1]: 1.0 mL of 5-TIA (0.20M) solution in *N*,*N*-dimethylformamide (DMF) was taken in a 5 mL vial. 0.5 mL of $Mn(NO_3)_2$ •xH_2O solution (0.20 M) in DMF was added to this solution. The vial was capped and heated to 85 °C for 72 h. The mother liquor was decanted and the Rectangular golden color crystals were filtered off, washed with DMF. The unreacted ligand can be removed by washing in DMF (3 mL, 4 times) as 5-TIA is highly soluble in DMF and afterwards resulting MOF was dried in air (10 min). [**Yield:** 70 %, 0.0130 gm depending on $Mn(NO_3)_2$• xH_2O]. ***FT-IR:*** (KBr 4000-600 cm^{-1}): 3448(m, br), 2929(w), 2867(w), 1652(s), 1505(w), 1383(s), 1250(m), 1092(s), 780(m), 708(m), 656(m) cm^{-1}.

Element analysis of evacuated Mn-5TIA-1: Found (%) C= 44.42, H= 3.37, N= 15.82; Calc. (%) C= 43.46, H= 3.36, N= 15.59.

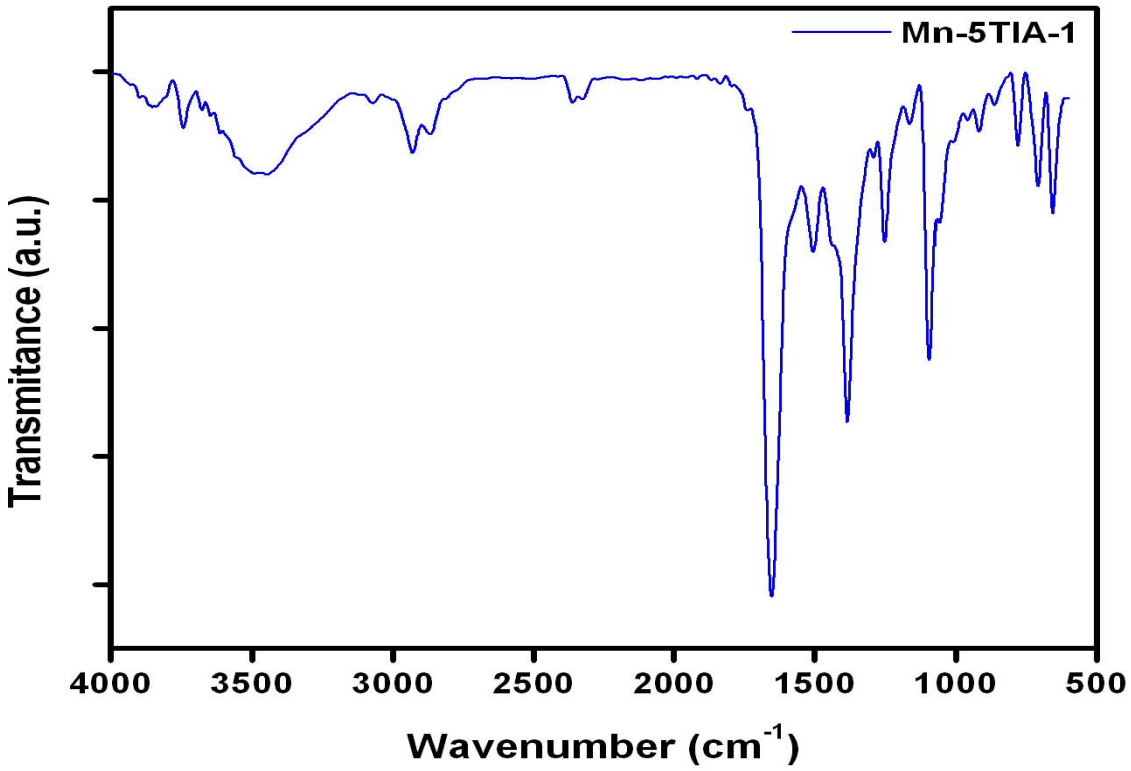

Figure S2. IR absorption spectrum of Mn-5TIA-1

Mn(5-TIA) [Mn-5TIA-2]: 1.0 mL of 5-TIA (0.20M) solution in *N*,*N*-dimethylformamide (DMF) was taken in a 5 mL vial. 0.5 mL of $Mn(NO_3)_2$ •xH_2O solution (0.20 M) in DMF and 0.5 mL of pyrazine solution (0.20 M) in DMF was added to this solution. The vial was capped and heated to 85 °C for 72 h. The mother liquor was decanted and the square yellow color crystals were filtered off, washed with DMF) and dried in air (10 min). [**Yield:** 74 %, 0.0074 gm depending on $Mn(NO_3)_2$• xH_2O]. ***FT-IR:*** (KBr 4000-600 cm^{-1}): 2980(m), 2308(m), 1654(s), 1367(s), 1091(m), 774(m), 711(m), cm^{-1}.

Element analysis of evacuated Mn-5TIA-2: Found (%) C= 40.83, H= 1.77, N= 14.828; Calc. (%) C= 41.98, H= 1.76, N= 14.68.

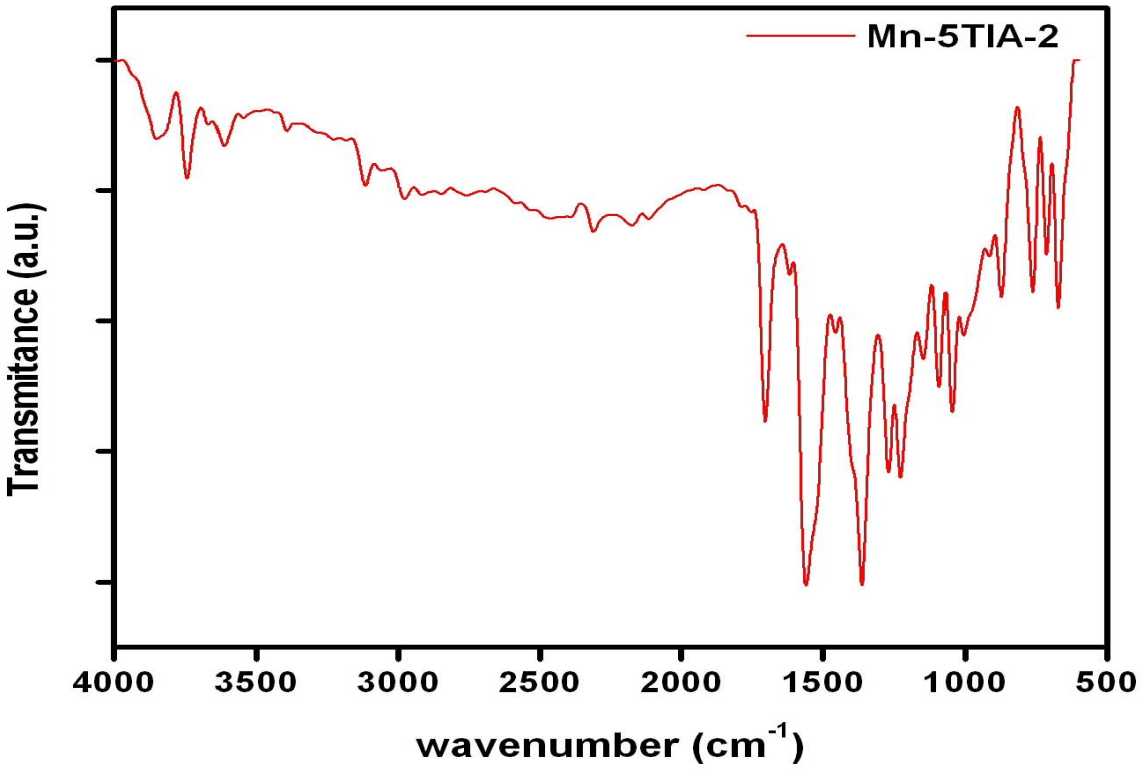

Figure S3. IR absorption spectrum of Mn-5TIA-2

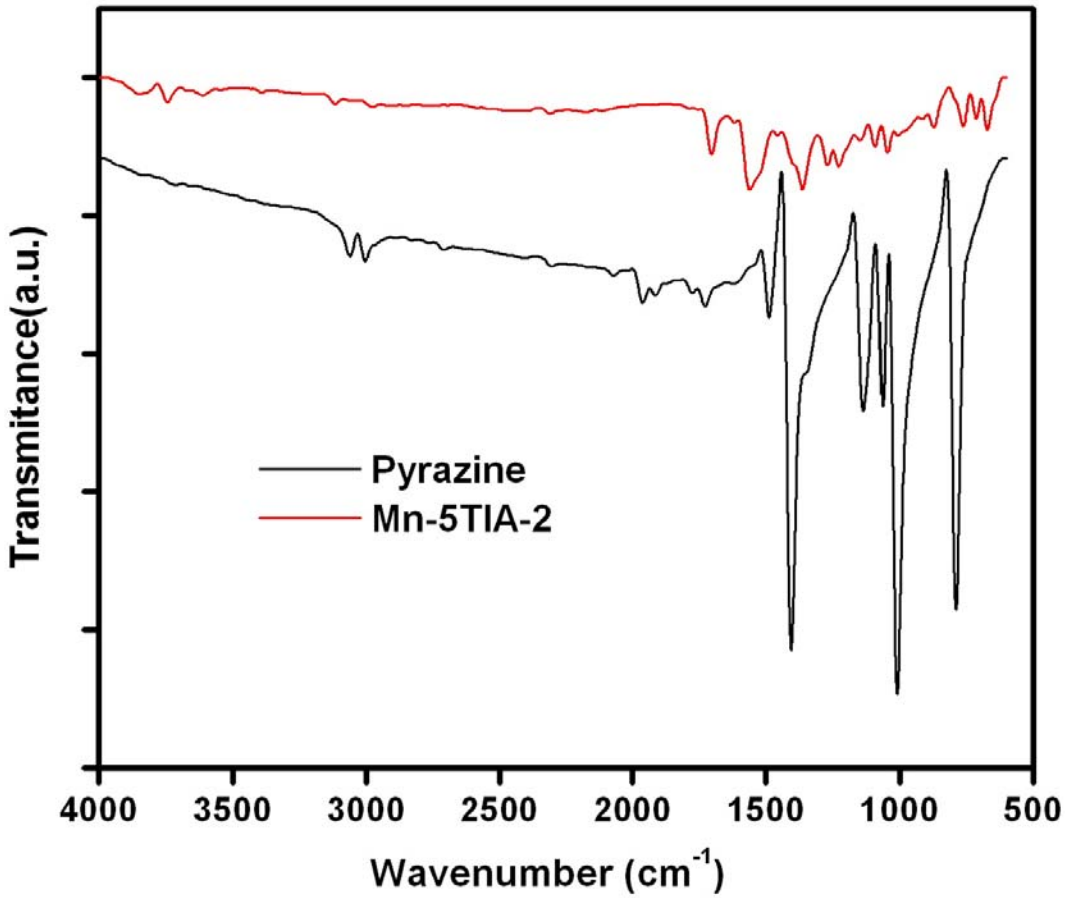

Figure S4. IR absorption spectrum of Mn-5TIA-2 and pyrazine

In Pyrazine IR peak around 3200 are probably **H-C**=N and **H-C**=C stretching (although 3200 is pretty high, but it may just because of the Nitrogen in the ring) which is absence in Mn-5TIA-2 confirms that there is no trapped guest pyrazine inside the pores in Mn-5TIA-2.

Mn(5-TIA) (Mn-5TIA-3): 1.0 mL of 5-TIA (0.20M) solution in *N*,*N*-dimethylformamide (DMF) was taken in a 5 mL vial. 0.5 mL of $Mn(NO_3)_2 \cdot 3H_2O$ solution (0.20 M) in DMF and 0.5 mL of 4, 4' bipyridine solution (0.20 M) in DMF was added to this solution. The vial was capped and heated to 85 °C for 72 h. The mother liquor was decanted and the rectangular colorless crystals were filtered off, washed with

DMF) and dried in air (10 min). [**Yield:** 74 %, 0.0074 gm depending on $Mn(NO_3)_2 \cdot xH_2O$]. ***FT-IR:*** (KBr 4000-600 cm^{-1}): 3524(m, br), 2929(m), 1654(s), 1052(w), 1384(s), 1254(m), 1091(s), 776(w), 712(w), 658(s), cm^{-1}.

Element analysis of evacuated Mn-5TIA-3: Found (%) C= 40.82, H= 1.77, N= 14.924; Calc. (%) C= 41.98, H= 1.76, N= 14.68.

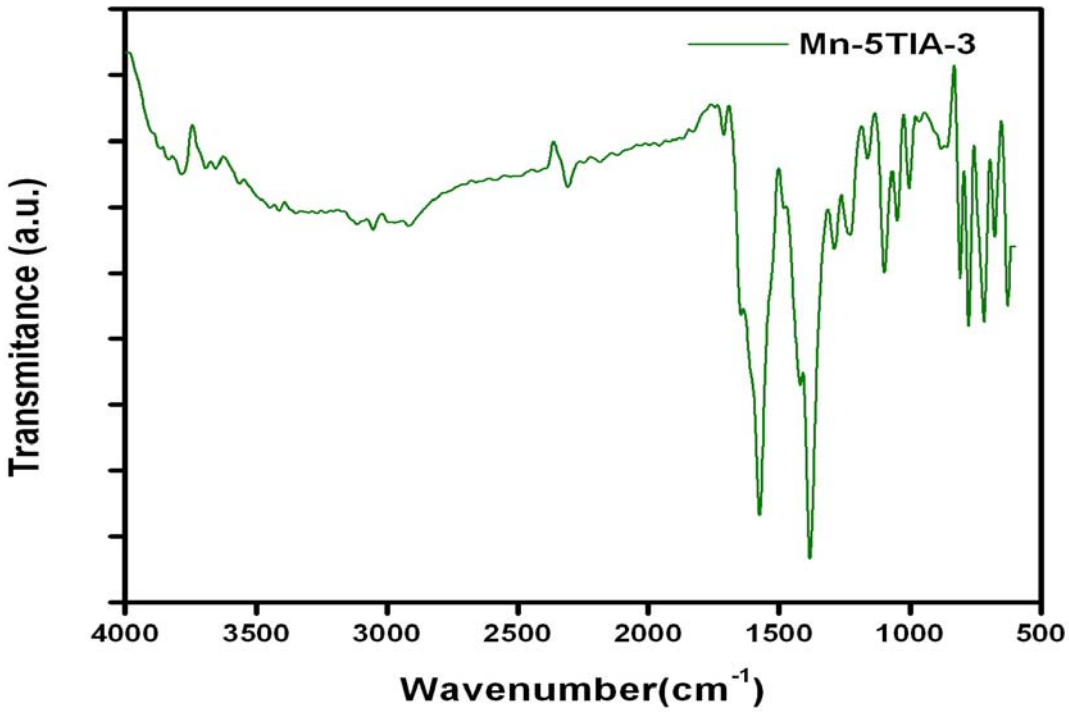

Figure S5. IR absorption spectrum of Mn-5TIA-3

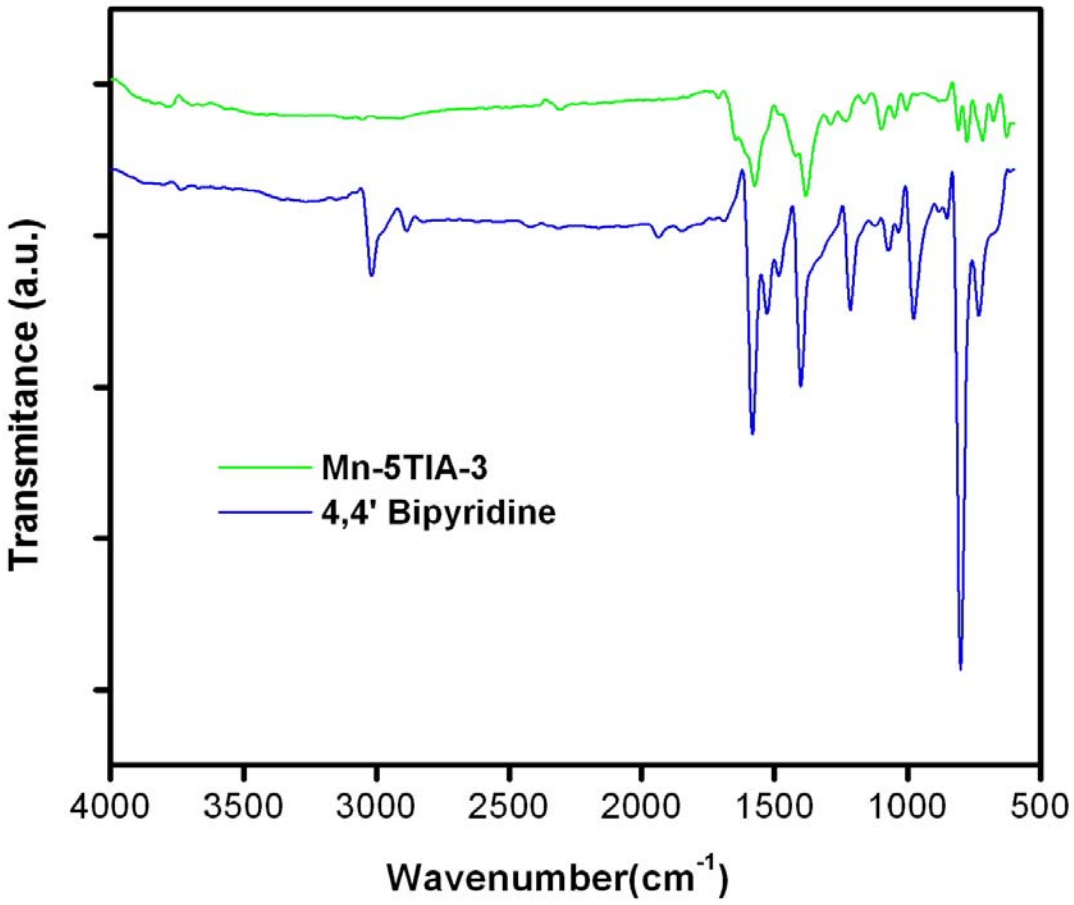

Figure S6.IR absorption spectrum of Mn-5TIA-3 and 4, 4'Bipyridine.

In 4, 4'Bipyridine IR peak around 3200 are probably **H-C**=N and **H-C**=C stretching (although 3200 is pretty high, but it may just because of the Nitrogen in the ring) which is absence in Mn-5TIA-3 confirms that there is no guest 4, 4'Bipyridine in Mn-5TIA-3.

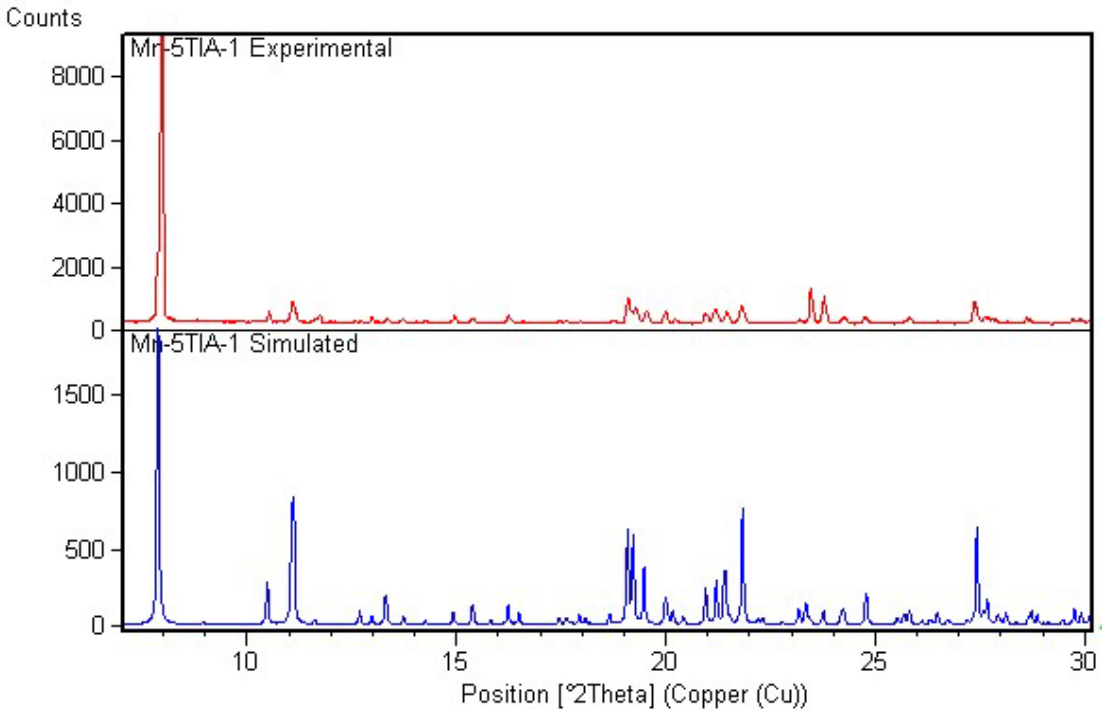

Figure S7. Comparison of the experimental PXRD pattern of as-prepared Mn-5TIA-1 (top) with the one simulated from its single crystal structure (bottom).

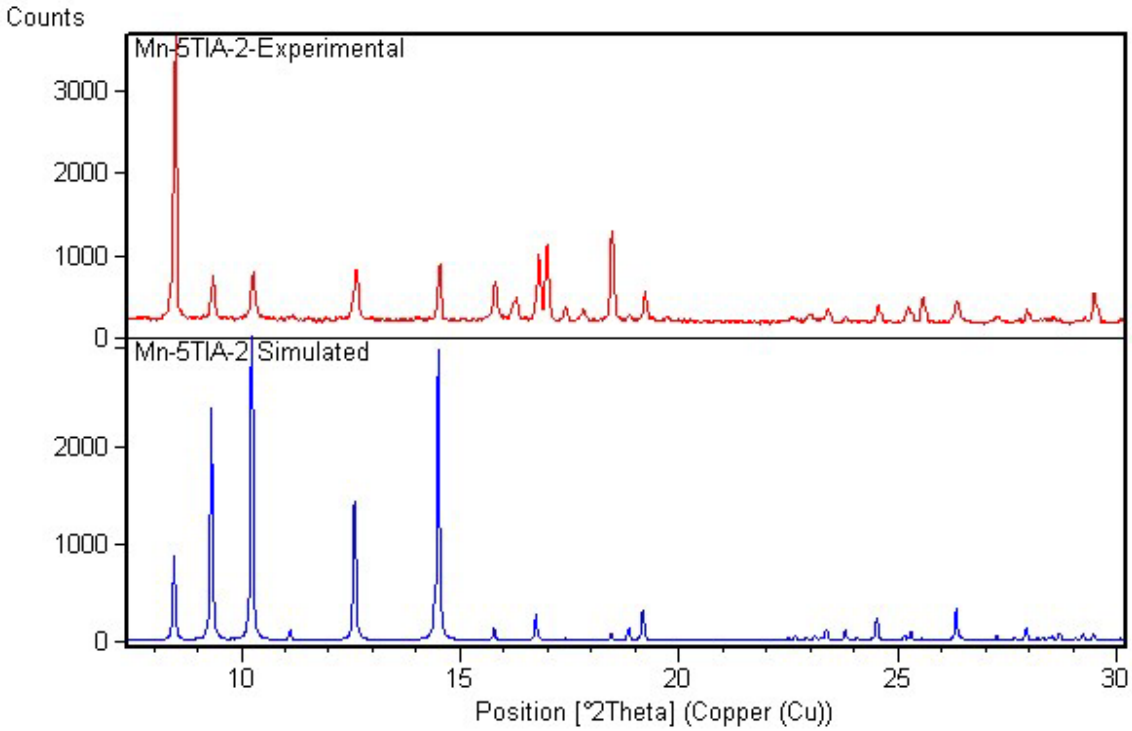

Figure S8. Comparison of the experimental PXRD pattern of as-prepared Mn-5TIA-2 (top) with the one simulated from its single crystal structure (bottom).

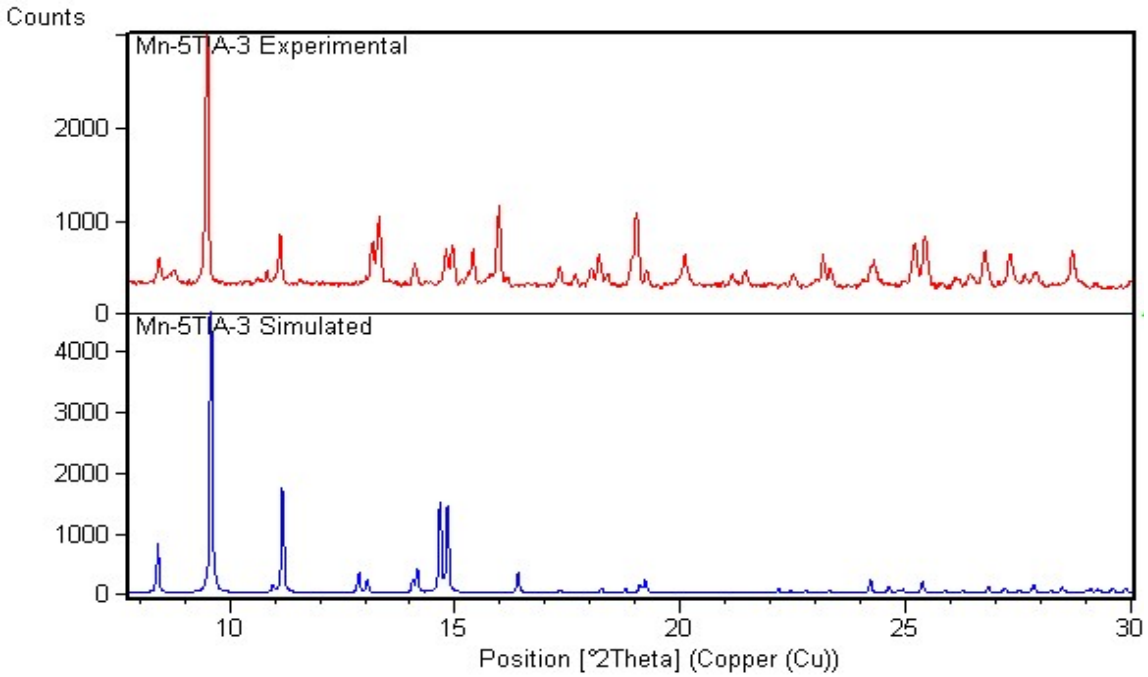

Figure S9. Comparison of the experimental PXRD pattern of as-prepared Mn-5TIA-3 (top) with the one simulated from its single crystal structure (bottom).

Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures.

General Data Collection and Refinement Procedures:

All single crystal data were collected on a Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo Kα radiation (λ=0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystals of the Mn-MOFs reported in the paper were mounted on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research).

Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. In every case frame widths of 0.5° were judged to be appropriate and full hemispheres of data were collected using the *Bruker SMART*[1] software suite. Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration and to check for rotational twinning using CELL_NOW[2]. In no data collection was evidence for crystal decay encountered. Following exhaustive review of the collected frames the resolution of the dataset was judged. Data were integrated using Bruker SAINT [3] software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data were subsequently corrected for absorption by the program

SADABS[4]. The space group determinations and tests for merohedral twinning were carried out using *XPREP*[3]. In all cases, the highest possible space group was chosen.

All structures were solved by direct methods and refined using the *SHELXTL 97*[5] software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final models were refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. Data were collected at 293(2)K for Mn-5TIA-2 MOF and 190(2)K for Mn-5TIA-1 and -2 MOFs presented in this paper. This lower temperature was considered to be optimal for obtaining the best data. Electron density within void spaces has not been assigned to any guest entity but has been modeled as isolated oxygen and/or carbon atoms. The foremost errors in all the models are thought to lie in the assignment of guest electron density. All structures were examined using the *Adsym* subroutine of PLATON[7] to assure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted otherwise. For all structures we note that elevated R-values are commonly encountered in MOF crystallography for the reasons expressed above by us and by other research groups.[8-17]

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Single crystal X-ray diffraction data of Mn-5TIA-1

A colorless type crystal (0.20× 0.16 × 0.12 mm^3) of Mn-5TIA-1 was mounted on 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a *SMART APEX* three circle diffractometer equipped with a CCD area detector (Bruker Systems Inc., 1999a)[19] and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_α radiation (λ=0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. A total of 32862 reflections were collected of which 6794 were unique and 6116 of these were greater than 2σ (*I*). The range of θ was from 1.85– 28.27^0. Analysis of the data showed negligible decay during collection. The structure was solved in monoclinic $P2_1/c$ space group, with Z = 4, using direct methods. All non-hydrogen atoms were refined anisotropically. Mn-5TIA-1 contains two 5-amino isophthalic acid molecule in the asymmetric unit. It should be noted that other supporting characterization data (*vide infra* Section S2) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0462 and wR_2 = 0.1024 (all data) with GOF = 1.157. Table S1 contains crystallographic data for the Mn-5TIA-1.

Table S1. Crystal data and structure refinement for Mn-5TIA-1

Empirical formula	C26 H24 Mn2 N8 O10
Formula weight	718.41
Temperature	190(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P21/c*
Unit cell dimensions	*a* = 10.7892(4) Å α = 90°
	b = 13.641(2) Å β = 95.049(2)°
	c = 19.851(3) Å γ = 90°
Volume	2910.2(7)
Z	4
Density (calculated)	1.640
Absorption coefficient	0.940
F(000)	1464
Crystal size	0.34× 0.25 × 0.24 mm^3
Theta range for data collection	1.85– 28.27
Index ranges	-13 <= h <= 13, -18 <= k <= 17, -25 <= l <= 25
Reflections collected	32862
Independent reflections	6794
Completeness to theta = 26.02°	99 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6794 / 0 / 419
Goodness-of-fit on F^2	1.157
Final R indices [I>2sigma(I)]	R_1 = 0.0462, wR_2 = 0.1024
R indices (all data)	R_1 = 0.0530, wR_2 = 0.1057
Largest diff. peak and hole	0.577 and -0.302 e.$Å^{-3}$

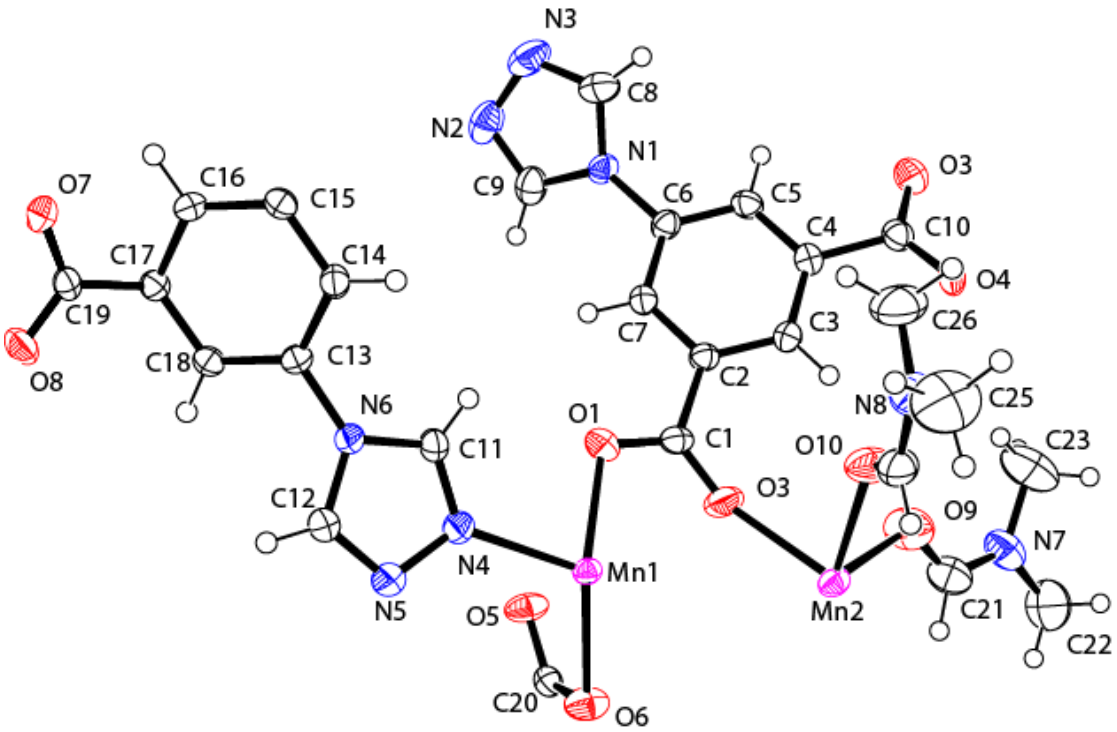

Figure S10. ORTEP drawing of the asymmetric unit of Mn-5TIA-1

Single crystal X-ray diffraction data of Mn-5TIA-2

A colorless type crystal (0.20× 0.16 × 0.12 mm^3) of Mn-5TIA-2 was mounted on 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a *SMART APEX* three circle diffractometer equipped with a CCD area detector (Bruker Systems Inc., 1999a)[19] and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_α radiation (λ=0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. A total of 9625 reflections were collected of which 3380 were unique and 2380 of these were greater than 2σ (*I*). The range of θ was from 2.89– 25.00^0. Analysis of the data showed negligible decay during collection. The structure was solved in orthorhombic *Pbcn* space group, with $Z = 4$, using direct methods. All non-hydrogen atoms were refined anisotropically. Mn-5TIA-2 contains one 5-amino isophthalic acid molecule in the asymmetric unit.

The attempts made to model the guests (solvent molecules) did not lead to identification of guest entities in these structures due to the limited periodicity of the solvent molecules in the crystals. Since the solvent is neither bonded to the framework nor tightly packed into the voids, solvent disorder can be expected for the MOF structures. Thus, electron density within void spaces which could not be assigned to any definite guest entity was modeled as isolated carbon or oxygen atoms, and the foremost errors in all the models lie with the assignment of guest electron density. To assess the correctness of the atomic positions in the framework, the application of the SQUEEZE routine of A. Spek has been performed. However, atomic co-ordinates for the "non-SQUEEZE" structures are also presented. It should be noted that the precision of this model is low; however, the structure is reported to demonstrate the nature of the framework of Mn-5TIA-2. Other

supporting characterization data (*vide infra* Materials and Methods) agree with the structure. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0862$ and $wR_2 = 0.2761$ (all data) with GOF = 1.147. Table S2 contains crystallographic data for the Mn-5TIA-2.

Table S2. Crystal data and structure refinement for Mn-5TIA-2(semiporous)

Empirical formula	C43.70 H10 Mn2 N6 O8
Formula weight	856.86
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	a = 12.2862(4) Å α = 90° b = 14.9471(4)Å β = 90° c = 20.8959(5) Å γ = 90°
Volume	3837.39(19)
Z	4
Density (calculated)	1.483
Absorption coefficient	0.722
F(000)	1712
Crystal size	0.20 × 0.17 × 0.12 mm^3
Theta range for data collection	2.89 – 25.00
Index ranges	-8 <= h <= 14, -17 <= k <= 11, -24 <= l <= 12
Reflections collected	9625
Independent reflections	3380
Completeness to theta = 26.02°	99.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3380 / 0 / 218
Goodness-of-fit on F^2	1.147
Final R indices [I>2sigma(I)]	R_1 = 0.0862, wR_2 = 0.2761
R indices (all data)	R_1 = 0.1098, wR_2 = 0.2872
Largest diff. peak and hole	1.002and 1.002 e.$Å^{-3}$

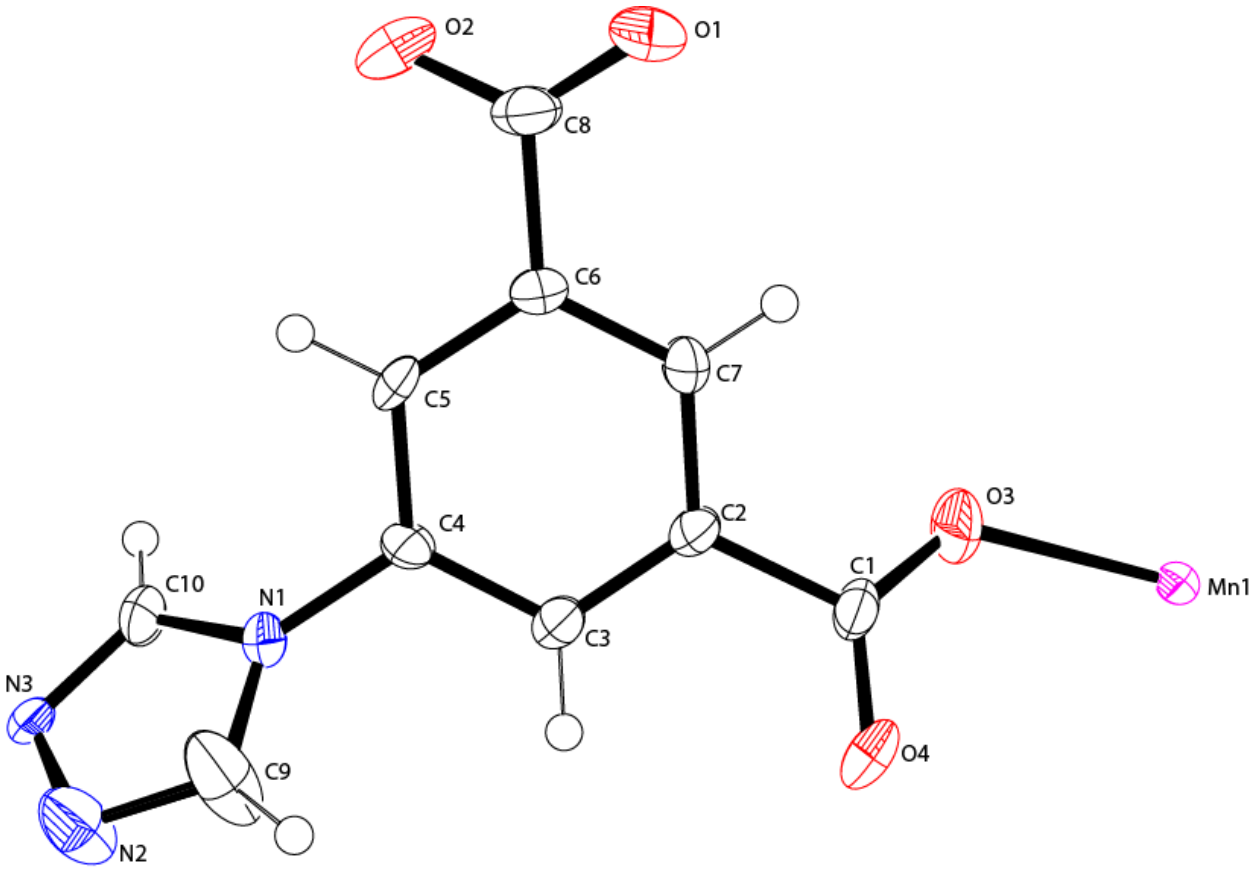

Figure S11. ORTEP drawing of the asymmetric unit of Mn-5TIA-2

Single crystal X-ray diffraction data of Mn-5TIA-3

A colorless type crystal (0.20× 0.16 × 0.12 mm^3) of Mn-5TIA-3 was mounted on 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a *SMART APEX* three circle diffractometer equipped with a CCD area detector (Bruker Systems Inc., 1999a)[19] and operated at 1500 W power (50 kV, 30 mA) to generate Mo K_α radiation (λ=0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. A total of 20465 reflections were collected of which 4436 were unique and 3554 of these were greater than 2σ (*I*). The range of θ was from 1.93 – 28.26^0. Analysis of the data showed negligible decay during collection. The structure was solved in monoclinic $P2_1/c$ space group, with Z = 4, using direct methods. All non-hydrogen atoms were refined anisotropically. Mn-5TIA-3 contains one 5-amino isophthalic acid molecule in the asymmetric unit. It should be noted that other supporting characterization data (*vide infra* Section S2) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to R_1 = 0.0642 and wR_2 = 0.15991 (all data) with GOF = 0.997 Table S3 contains crystallographic data for the Mn-5TIA-3.

Table S3. Crystal data and structure refinement for Mn-5TIA-3 (porous)

Empirical formula	C10 H5 Mn N3 O4
Formula weight	286.11
Temperature	190(2)K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P21/c*
Unit cell dimensions	a = 11.214(11) Å α = 90°
	b = 12.585(13) Å β = 110.125(15)°
	c = 14.447(15) Å γ = 90°
Volume	1914(3)
Z	4
Density (calculated)	0.993
Absorption coefficient	0.695
F(000)	572
Crystal size	0.25 × 0.21 × 0.18 mm^3
Theta range for data collection	1.93 – 28.26
Index ranges	-14 <= h <= 14, -16 <= k <= 15, -18 <= l <= 18
Reflections collected	20465
Independent reflections	4436
Completeness to theta = 26.02°	99.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4436 / 0 / 158
Goodness-of-fit on F^2	0.997
Final R indices [I>2sigma(I)]	R_1= 0.0642, wR_2 = 0.1599
R indices (all data)	R_1 = 0.0778, wR_2 = 0.1669
Largest diff. peak and hole	1.325and -0.499 e.$Å^{-3}$

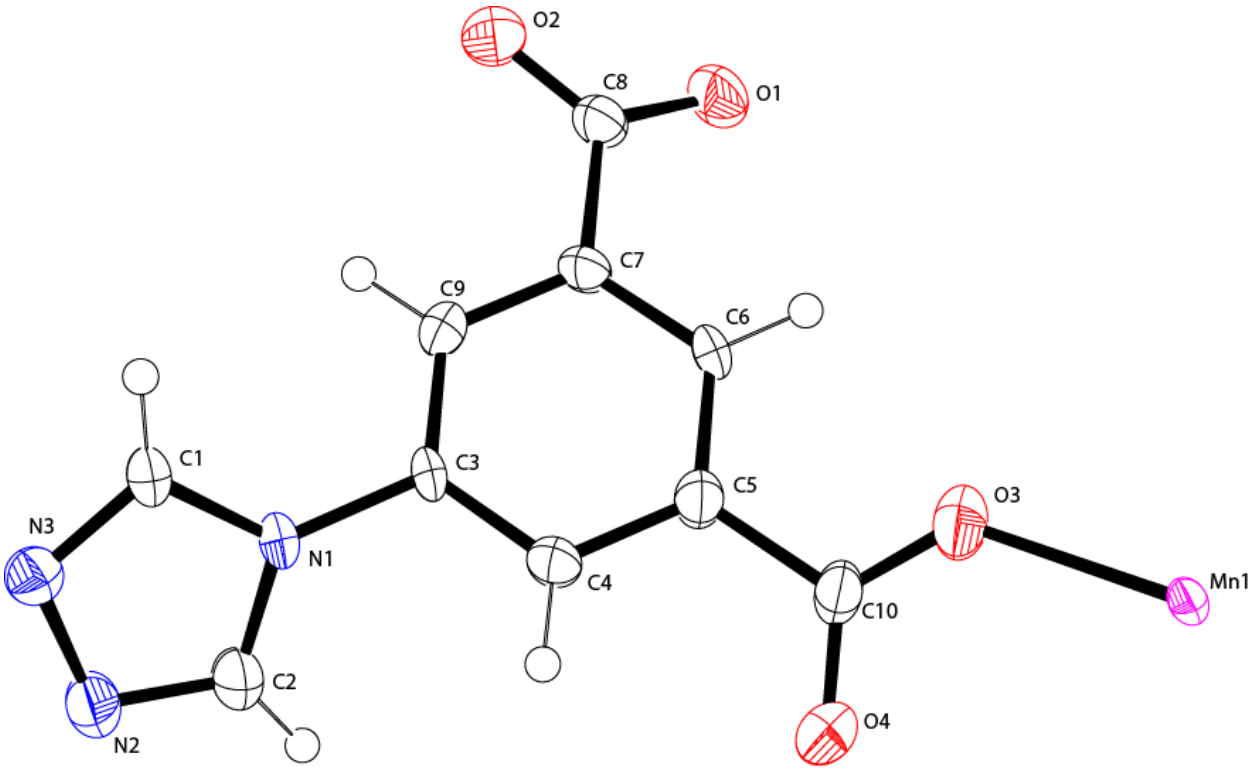

Figure S12. ORTEP drawing of the asymmetric unit of Mn-5TIA-3

Section S3. Thermo Gravimetric analysis of Mn-MOFs

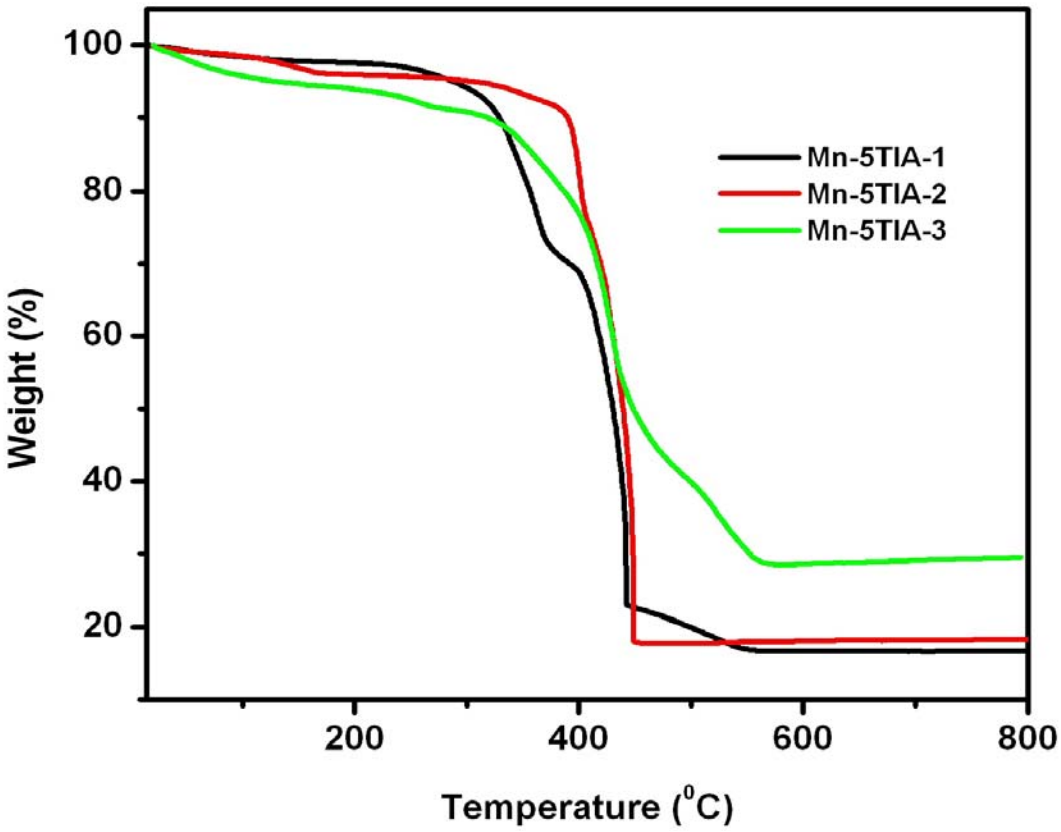

Figure S13. Overlay of TGA traces of as-synthesized Mn-5TIA-1(black), Mn-5TIA-2 (red), and Mn-5TIA-3 (green) samples.

Section S4. Gas Adsorption analysis of Mn-MOFs

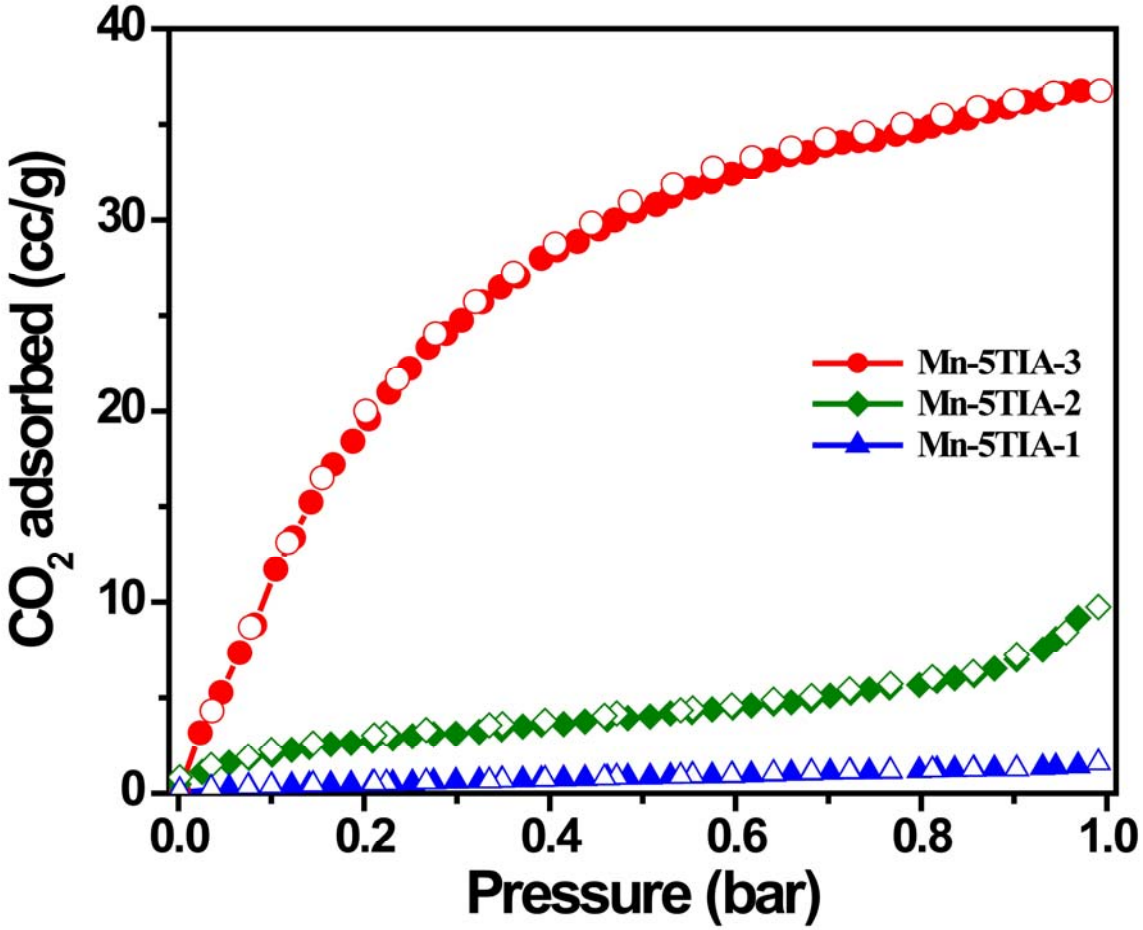

Figure S14. The CO_2 gas-sorption isotherms for Mn-5TIA-1 -2 and -3 measured at 298 K. The filled and open circles represent adsorption and desorption branches, respectively.

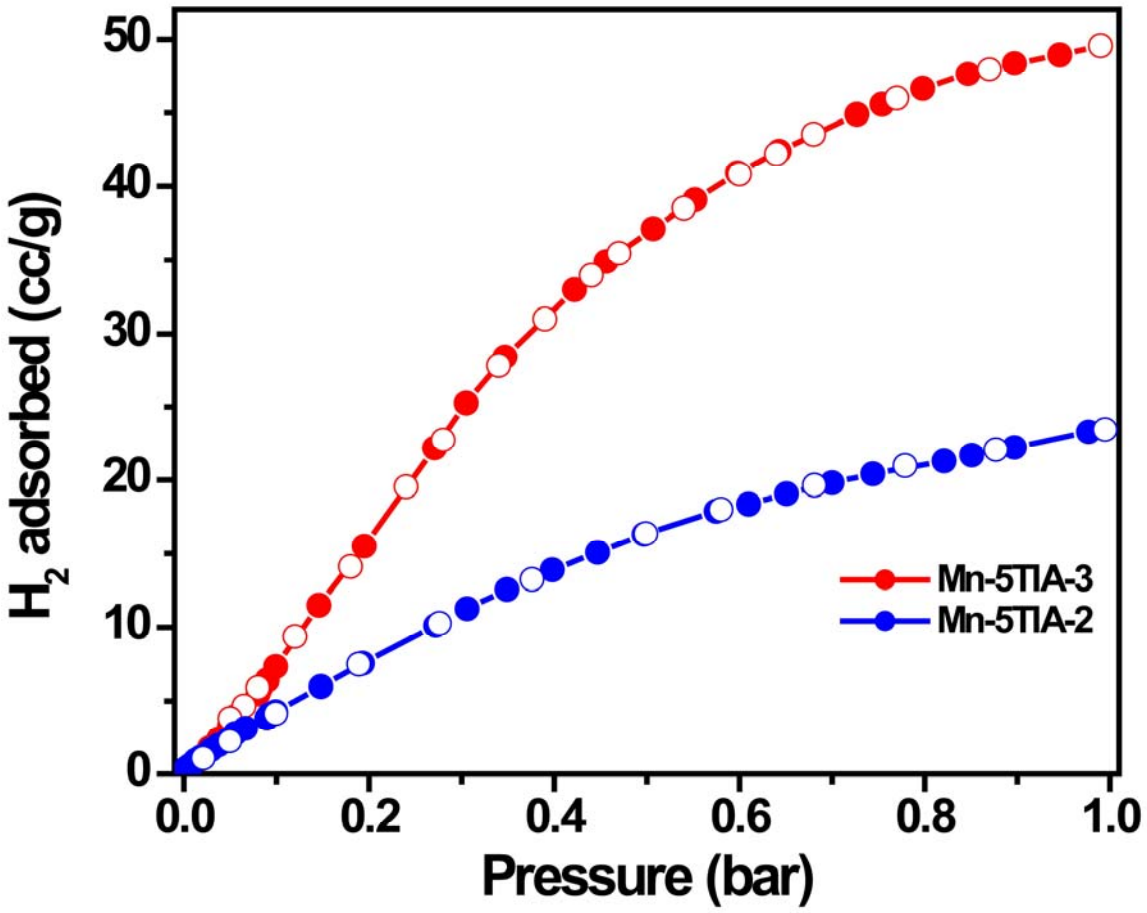

Figure S15. The H_2 gas-sorption isotherms for Mn-5TIA -2 and -3 measured at 77 K. The filled and open circles represent adsorption and desorption branches, respectively.

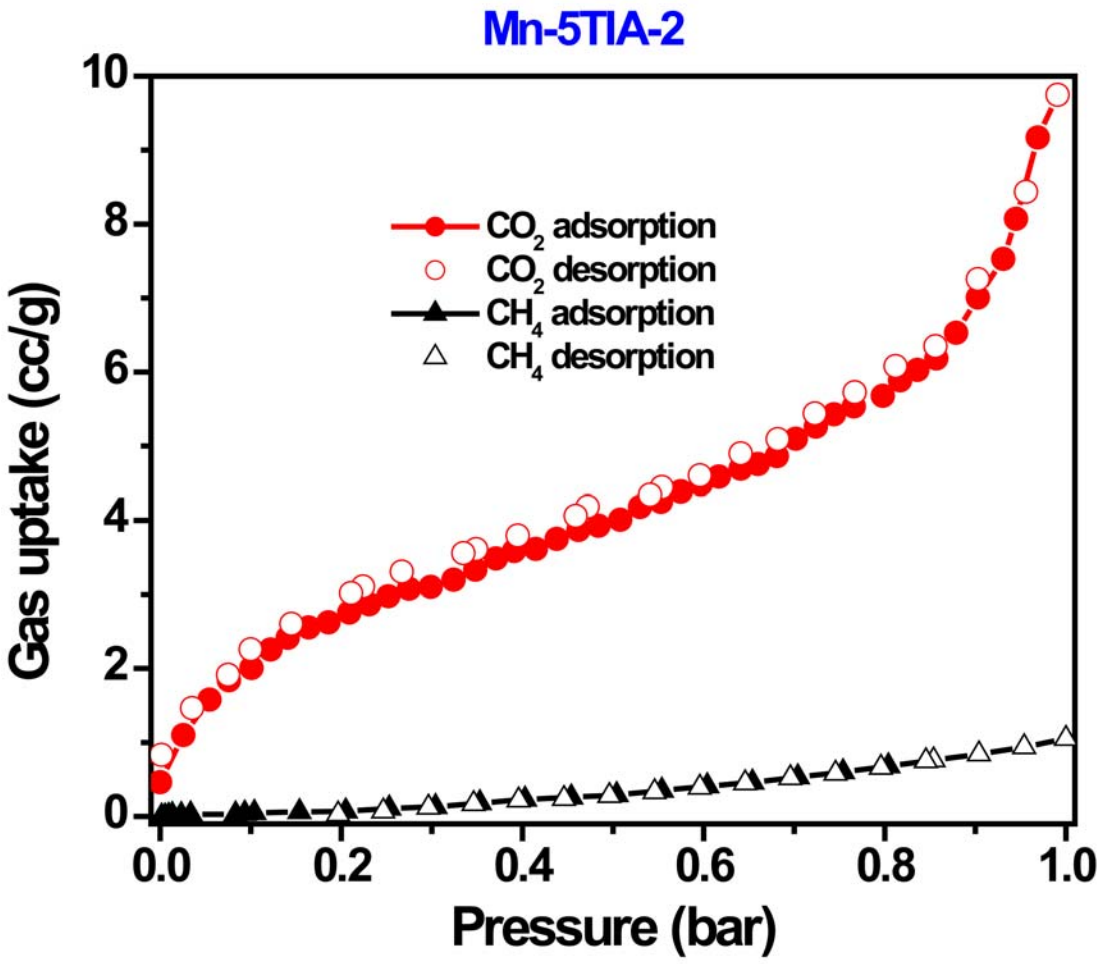

Figure S16. Comparison of CO_2 and CH_4 gas-sorption isotherms for Mn-5TIA -2 measured at 298 K. The filled and open circles represent adsorption and desorption branches, respectively.

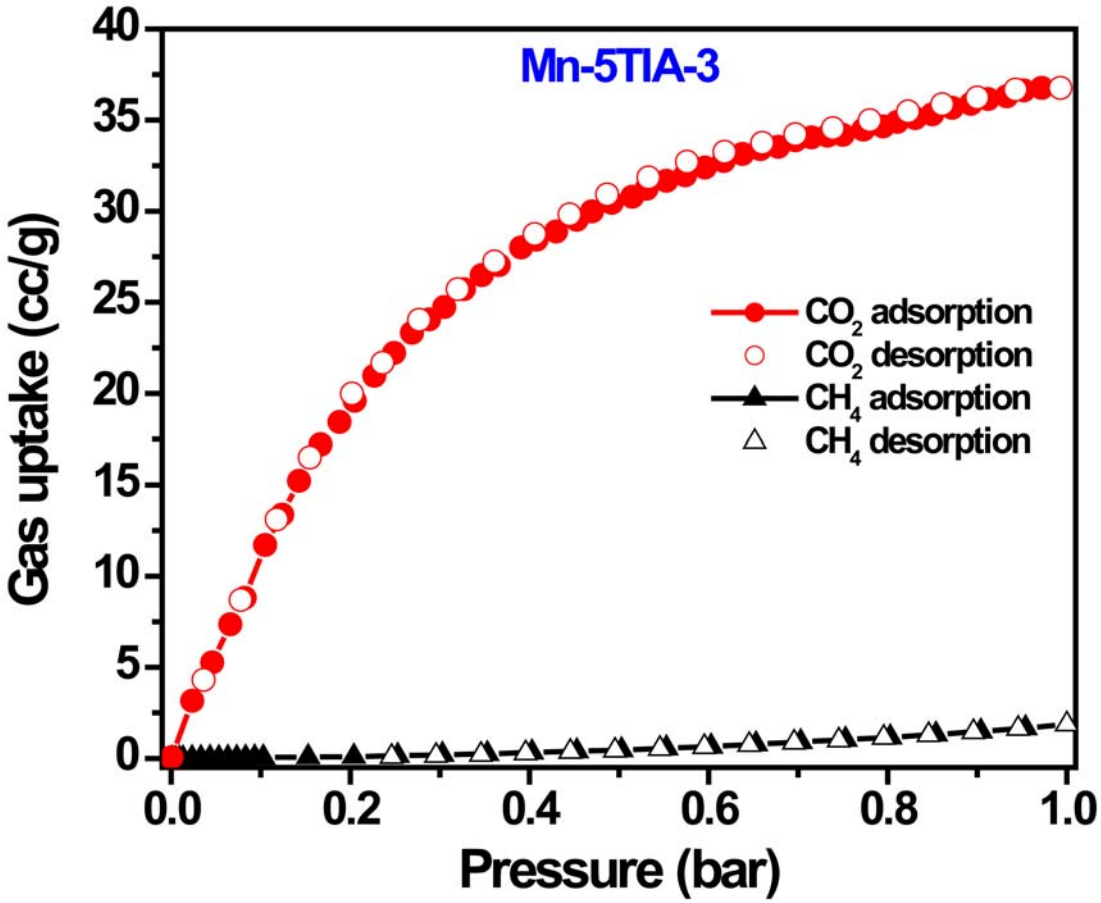

Figure S17. Comparison of CO_2 and CH_4 gas-sorption isotherms for Mn-5TIA -3 measured at 298 K. The filled and open circles represent adsorption and desorption branches, respectively.

Section S5. Single crystal structures of Mn-MOFs:

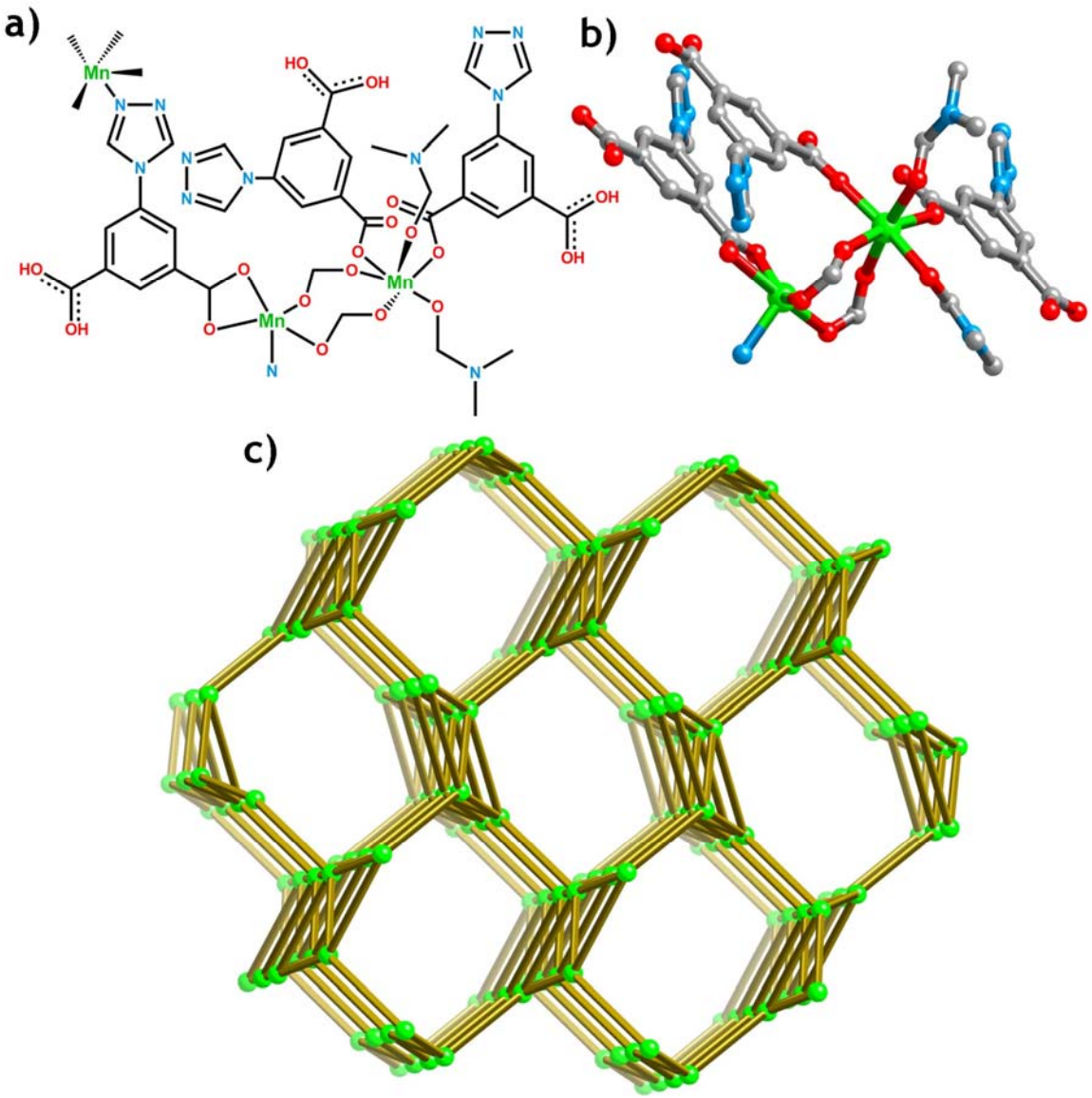

Figure S18. Crystal structure of Mn-5TIA-1 a) Coordination of 5-TIA with metal center b) Ball and stick model of coordination, Solvent molecules are omitted for clarity c) Metal connection. Color code: Mn (green), N (blue), O (red), C (black), H (pink).

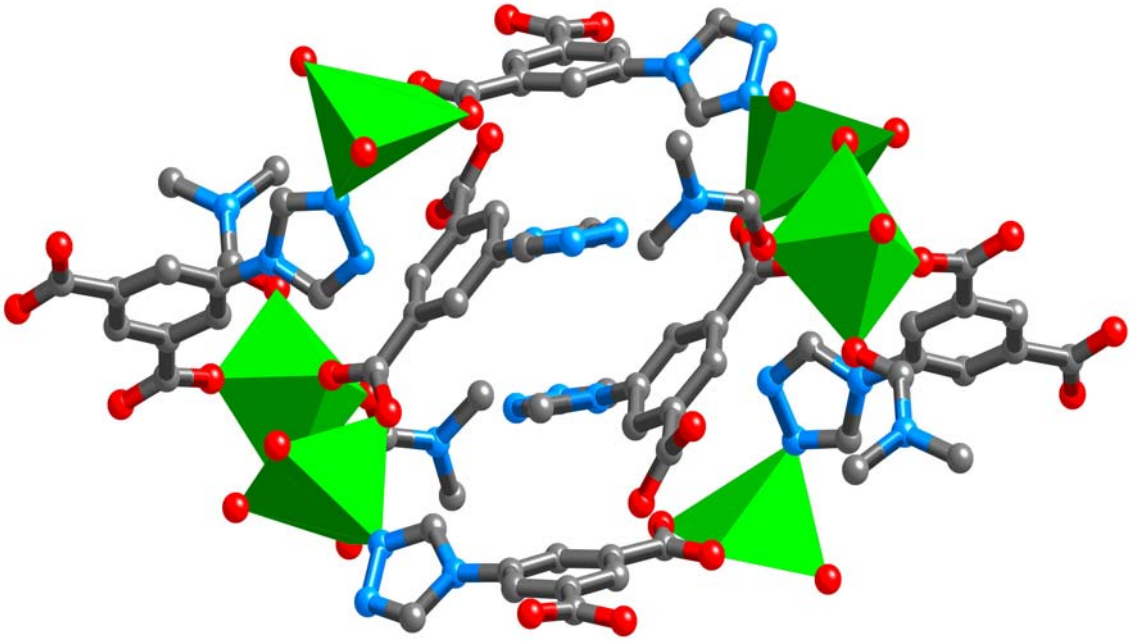

Figure S19. Packing diagram of Mn-5TIA-1 showing different modes of attachments of metal centers with ligand 5-TIA through *b* axis. Hydrogen atoms are omitted for clarity. Color code: Mn (green), N (blue), O (red), C (black).

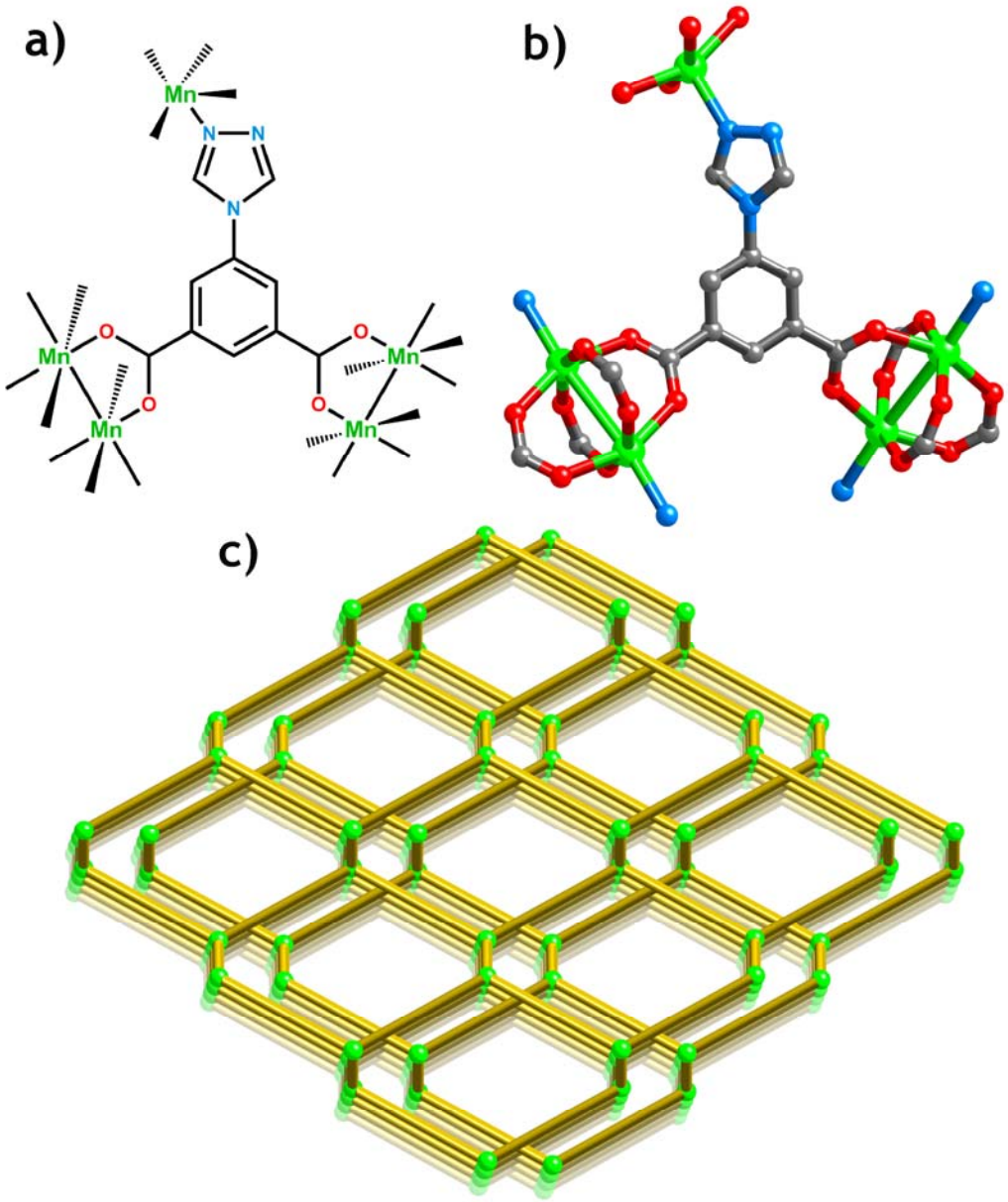

Figure S20. Crystal structure of Mn-5TIA-2. a) Coordination of 5-TIA with metal center b) Ball and stick model, Solvent molecules are omitted for clarity c) Metal connection. Color code: Mn (green), N (blue), O (red), C (black),

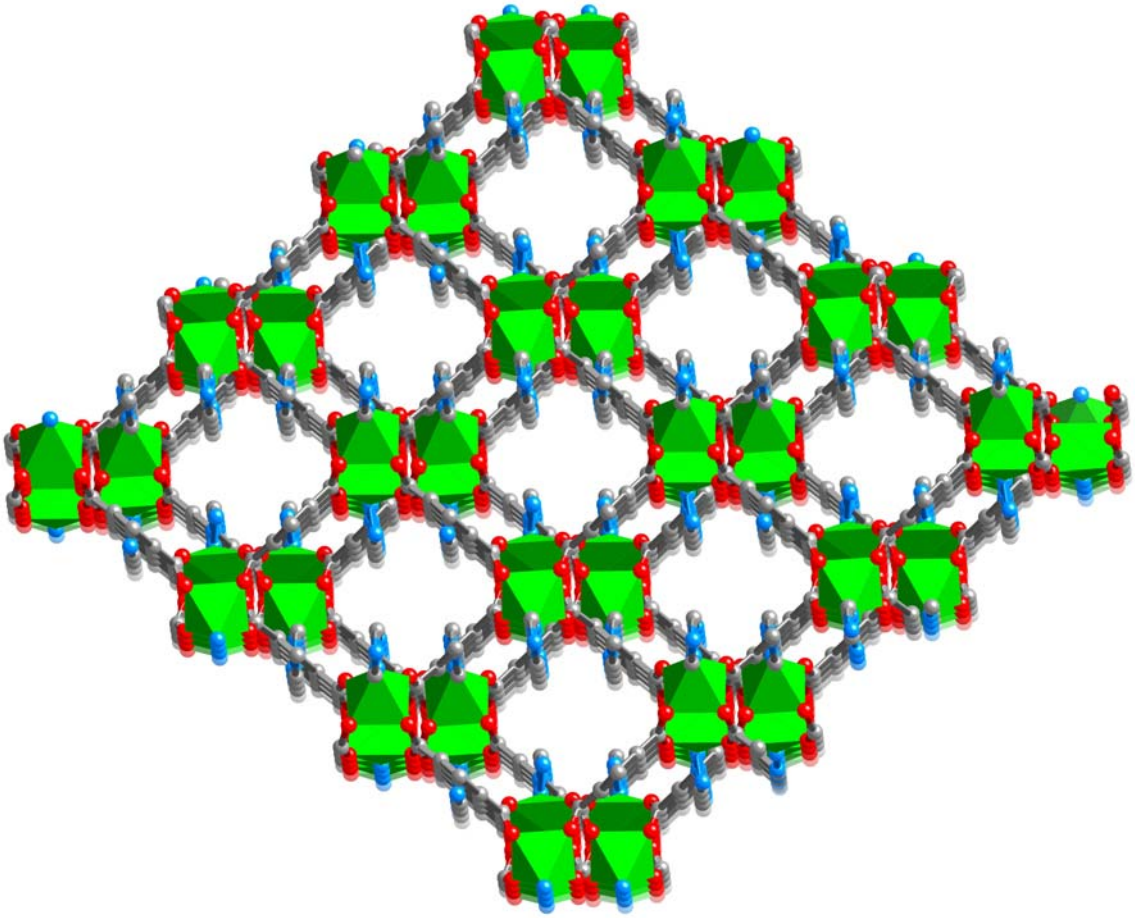

Figure S21. Packing diagram of Mn-5TIA-2 showing one dimensional pores of 2.57 Å × 2.57Å through c axis. Hydrogen atoms are omitted for clarity. Color code: Mn (green), N (blue), O (red), C (black).

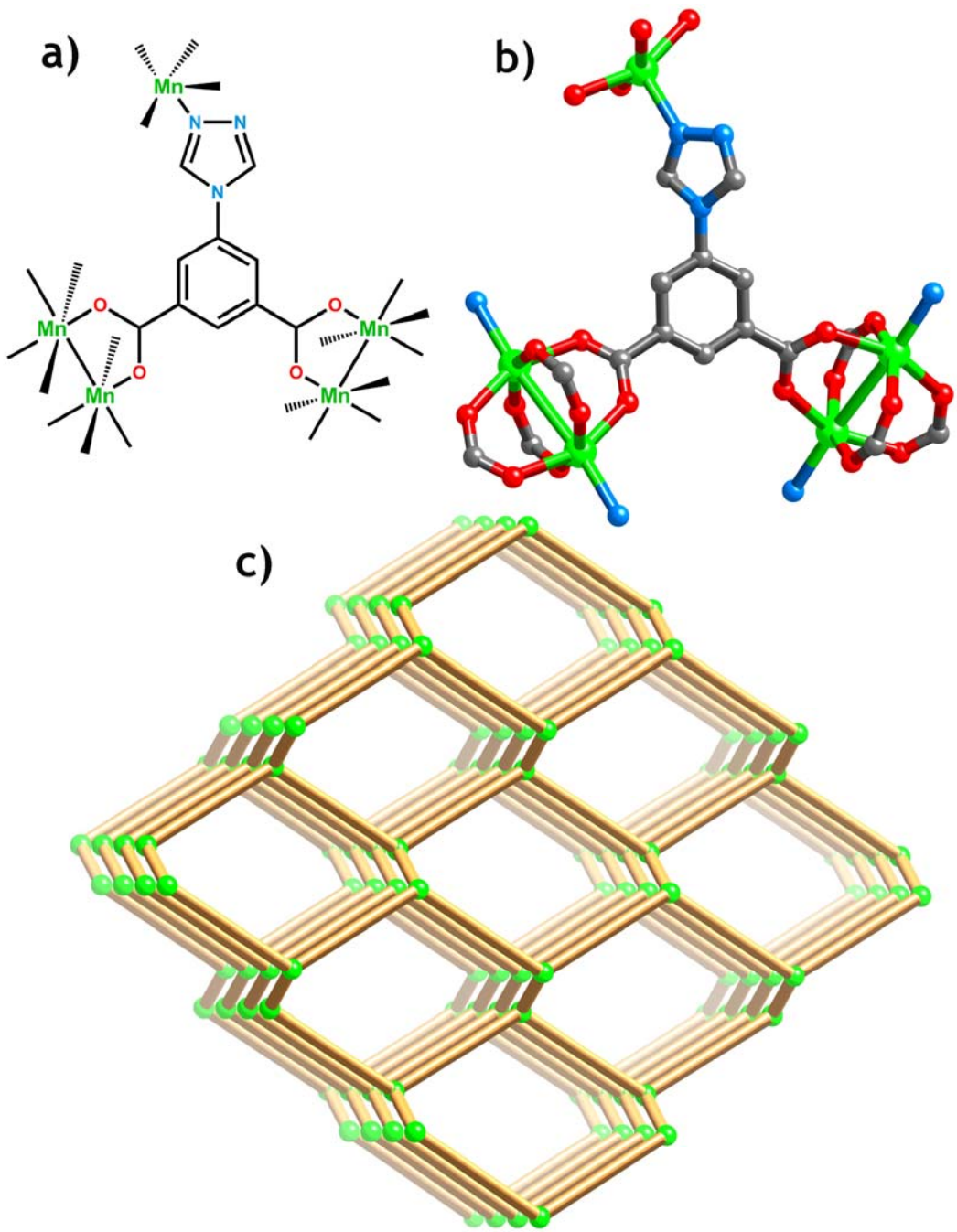

Figure S22. Crystal structure of Mn-5TIA-3. a) Coordination of 5-TIA with metal center b) Ball and stick model, Solvent molecules are omitted for clarity c) Metal connection. Color code: Mn (green), N (blue), O (red), C (black),

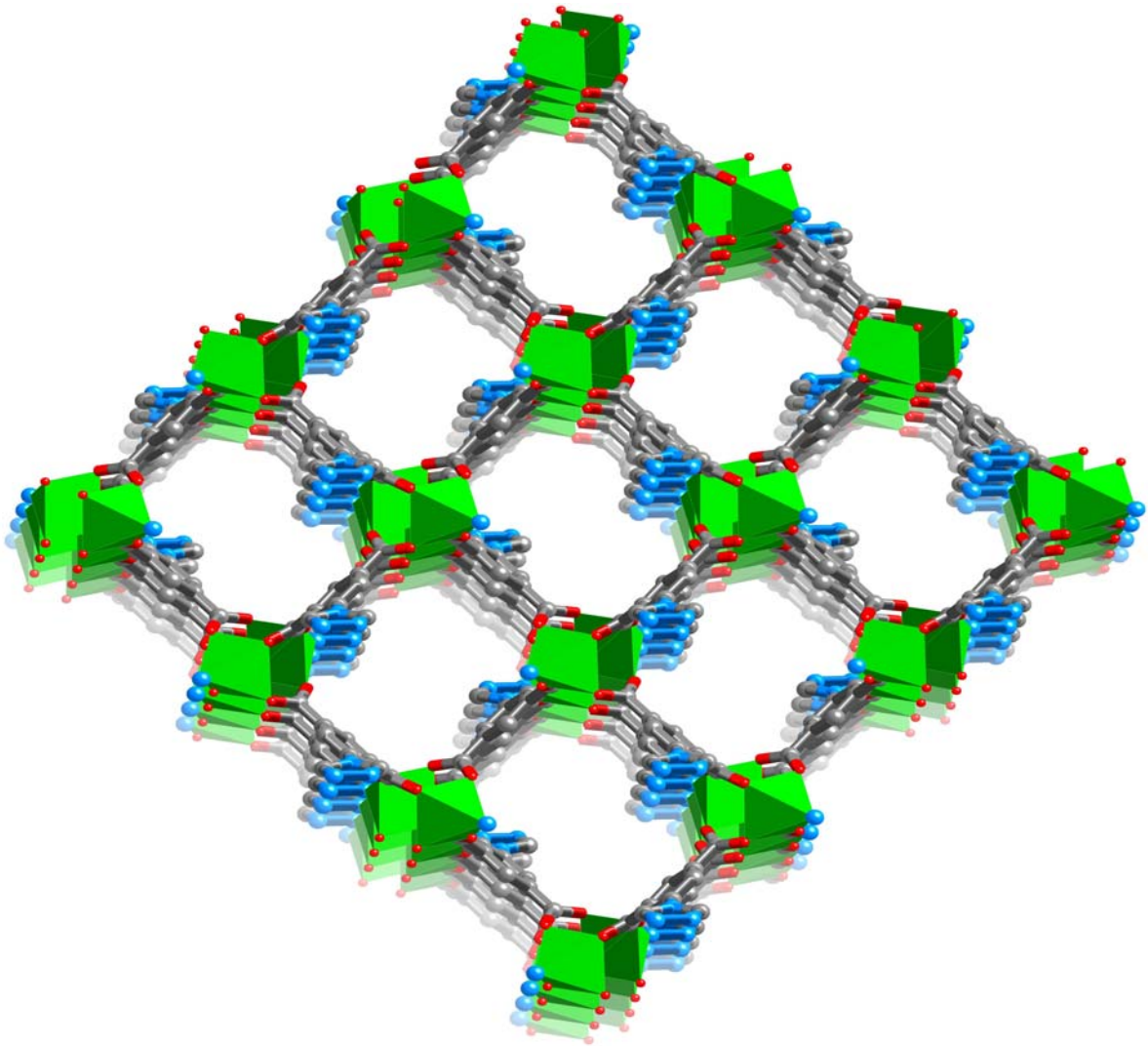

Figure S23. Packing diagram of Mn-5TIA-3 showing one dimensional pores of 7.22Å × 2.80 Å through a axis. Hydrogen atoms are omitted for clarity. Color code: Mn (green), N (blue), O (red), C (black).

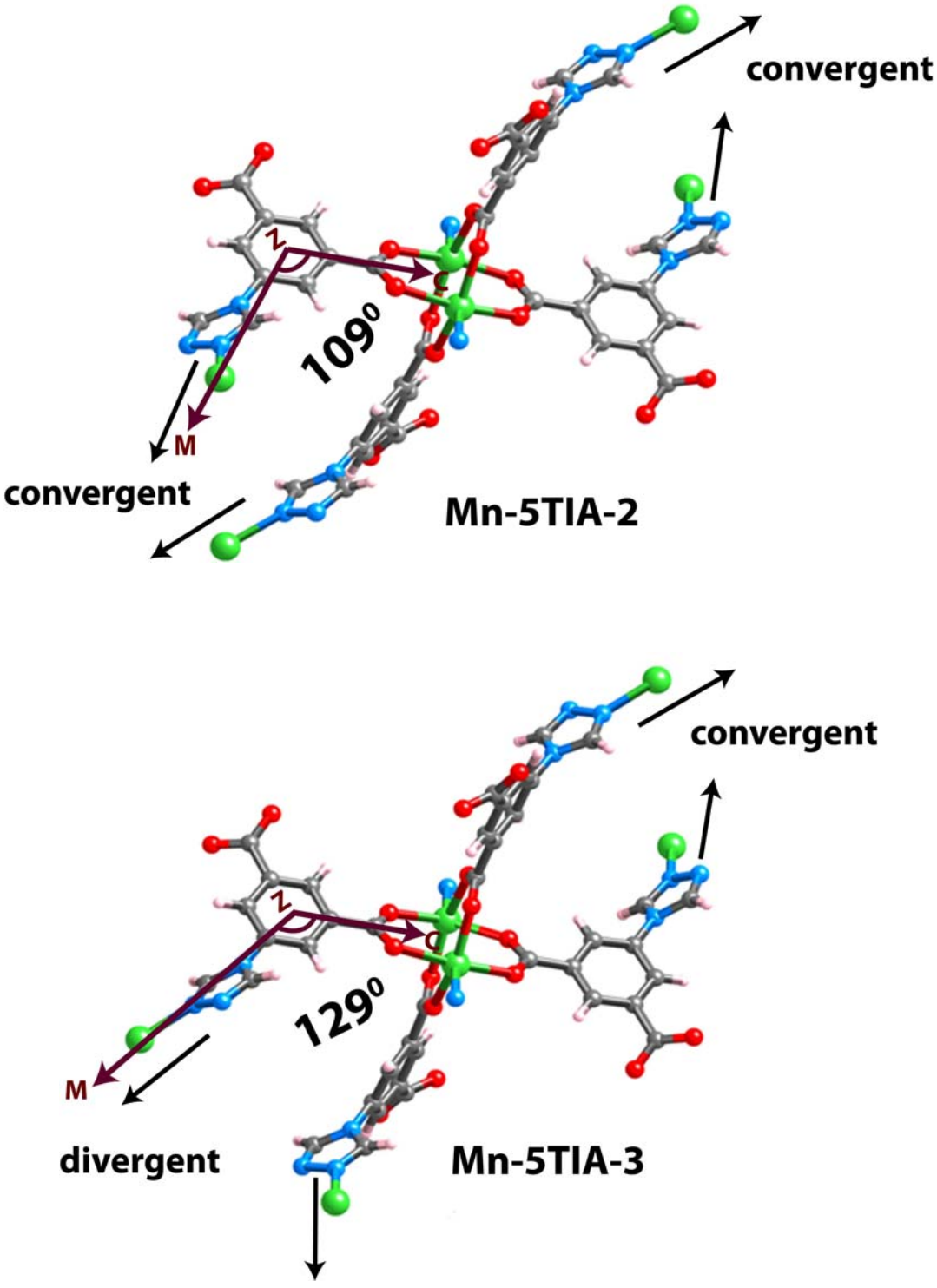

Figure S24. (Top) Mn-5TIA-2 the coordination of μ_1-triazolyl nitrogen functionality to the Mn(II) metal is convergent on both sides of the diamanganese paddlewheel SBU. (Bottom) The coordination of μ_1-triazolyl nitrogen functionalities to the Mn (II) metal in Mn-5TIA-3 is convergent on one side and divergent on the other side of the diamanganese paddlewheel SBU.