## **Supporting Information for:**

## Site-Specific Metal and Ligand Substitutions in a Microporous Mn<sup>2+</sup>-Based Metal-Organic Framework

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Fig. S1 An optical image showing the as-synthesized form of the parent  $Mn_3L_3$  (L-based) material synthesized using a ratio of L:L' of 1:0.



**Fig. S2** An optical image showing the as-synthesized form of the mixed-linker material synthesized using a ratio of L:L' of 0.54:0.46.



**Fig. S3** An optical image showing the as-synthesized form of the L'-based material synthesized using a ratio of L:L' of 0:1.



**Fig. S4** An enlarged view of the methyl substituent located in the vicinity of the terminal  $Mn^{2+}$  ion of the trinuclear  $Mn_3^{6+}$  cluster. Upon substitution of the hydrogen atoms (solid spheres; Van der Vaals radius: 120 pm) with fluorine (transparent spheres; 135 pm), an unfavorable steric overlap occurs with the surrounding atoms, leading to the trifluoromethyl-substituted linker being predominantly located at the pillar linker sites. Purple spheres, grey, blue, and red nodes represent Mn, C, N, and O, respectively, while H atoms except on the trifluoromethyl substituent have been omitted for clarity.



Fig. S5 A view of the truncated trifluoromethyl-substituted bispyrazolate moiety as modelled by density functional theory at the m06/6-311G++ (d,p) level of theory (upper); and relative energies of the molecule at different angles of rotation about the methylene spacer (lower). Here, the energies are computed for a full, 360° rotation of  $\theta$  (formed by the four nitrogen atoms of the pyrazolate functionalities), calculating the energies every 20°. For the molecular system, the crystallographically-observed angle ( $\theta_0 = -155.6^\circ$ ,  $\Delta \theta = 0^\circ$ ) in the closed structure is found to be the most favorable conformation, with a local minimum observed for  $\Delta \theta$  in the range of 140-160° as observed in the open structure. The rotational barrier is significantly greater in the case of the trifluoromethyl-substituted L' linker, which is consistent with the higher pressures at which the structural reorganization is observed in the adsorption isotherms.



Fig. S6  $N_2$  adsorption isotherms recorded at 77 K for  $Mn_3L_3$  (red) and  $Mn_3L_{2.49}L'_{0.51}$  (blue).



Fig. S7 CO<sub>2</sub> adsorption isotherms recorded at 195 K for  $Mn_3L_3$  (red) and  $Mn_3L_{2.49}L'_{0.51}$  (blue).



Fig. S8  $H_2O$  adsorption isotherms recorded at 298 K for  $Mn_3L_3$  (red) and  $Mn_3L_{2.49}L'_{0.51}$  (blue).



Fig. S9 An optical image of crystals of the  $Mn_3L_3$  framework following metal exchange with FeCl<sub>2</sub>·4H<sub>2</sub>O.



Fig. S10 An optical image of crystals of the  $Mn_3L_3$  framework following metal exchange with FeCl<sub>3</sub>.

## Single crystal X-ray structure determinations on Fe-exchanged Mn<sub>3</sub>L<sub>3</sub> samples

Full spheres of diffraction data were collected for single crystals mounted on nylon loops in Paratone-N at 100 K on the MX1 beamline of the Australia Synchrotron,  $\lambda =$ 0.71073 Å.[1]  $N_{tot}$  reflections were merged to N unique ( $R_{int}$  quoted) after 'empirical'/multiscan absorption correction (proprietary software) and used in the full matrix least squares refinements on  $F^2$ ,  $N_0$  with  $F > 4\sigma(F)$  being considered 'observed'. Anisotropic displacement parameter forms were refined for the non-hydrogen atoms; hydrogen atoms were treated with a riding model [weights:  $(\sigma^2(F_0)^2 + (aP)^2 + (bP))^{-1}$ ;  $P = (F_0^2 + 2F_c^2)/3$ ]. Neutral atom complex scattering factors were used; computation used the *SHELXL2013* program.[2] Pertinent results are given in the manuscript and in Table S1. CIF data have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 1443923 ([Fe<sub>3</sub>(L<sub>3</sub>)]-FeCl<sub>3</sub>) and 1443924 ([Mn<sub>3-x</sub>Fe<sub>x</sub>(L<sub>3</sub>)]-FeCl<sub>2</sub>, x = 0.55).

*Variata*. In the crystal structure of  $[Fe_3(L_3)]$ ·FeCl<sub>3</sub> the metal node of the MOF was refined with an Fe<sub>3</sub> composition (with no allowance made in the refinement for the residual amount of Mn potentially remaining in the node). The MOF structure itself is well behaved with only limited disorder; the commonly encountered disorder of one of the phenyl rings of one of the ligand molecules (not the ligand that is metalated post-synthetically) in the asymmetric unit was refined with two major orientations (0.65:0.35 ratio). The post-synthetically added metal centre is not clearly resolved in this structure as  $F_{obs}$  maps reveal (see Figure S11). The metal site itself shows a region of diffuse electron density bounded by two additional regions of electron density in the 'axial' positions of a possible octahedral metal complex and a third region of electron density

not on the mirror plane. As noted, we have modelled the electron density as an octahedral Fe<sup>3+</sup> cation (due to slightly shorter Fe-N bonds of 2.084(8) Å) possessing two inner-sphere chloride ions and a third outer-sphere anion within the pores of the framework (see Fig. S11 below) but the disorder present limits ultimate confirmation and complete refinement. Residual electron density is located adjacent Fe(3) and Cl(1) with an unreasonably long Fe-Cl distance as a consequence of the apparent disorder. Two moderate peaks in the electron density different map located in the positons normally reserved for non-coordinated anions were refined as sites for the outer-sphere chloride ion with 0.2 occupancy each (both on a mirror plane); no additional positions were identified for the remaining 0.1 occupancy chloride to achieve charge balance.

In the refinement of  $[Mn_{3-x}Fe_x(L_3)]$ -0.4FeCl<sub>2</sub> (x = 0.55) the Fe occupancy of the metalation site was established by trial refinement and determined to be 0.2 (40% occupancy). Using this data and the Fe:Mn ratio for the material, established from inductively-coupled plasma mass spectrometry (ICP-MS), the composition of the metal node was set as  $Mn_{2.45}Fe_{0.55}$  and refined with fixed occupancy. Due to the metal occupancy of the bis-pyrazole metalation site only being 40%, meaning that 60% of the ligand does not have a metal centre, there is considerable disorder of the ligand. In other structures of this MOF (without metalation but in DMF and CH<sub>3</sub>CN)[3] we see distinct conformations for the non-coordinated ligand . Thus, for this structure, the low occupancy of the metal results in disorder for the bis-pyrazole binding site and the surrounding phenyl ring but the data was not of sufficient quality to allow this disorder to be modelled. Disorder of one of the phenyl rings of the other ligand molecule in the asymmetric unit was refined with two major orientations (0.77:0.23 ratio). The pores

of the MOF contain a number of isolated peaks that could not be modelled as solvent (ethanol due to sample preparation). A peak, assigned as a chloride (0.2 occupancy, 40%) to provide charge balance to added octahedral Fe centre, sits in the pocket typically occupied by anions within the MOF structure.[3] There is additional electron density in this 'anion binding' site (largest peak = 2.958 eÅ<sup>3</sup> before application of the SQUEEZE routine of Platon) but that data is not of sufficient quality for us to build a reasonable structural model for refinement. The SQUEEZE routine of Platon[4] was applied to the data to account for this residual electron density bringing about significant improvements in  $R_1$ ,  $wR_2$  and GOF.



**Figure S11**.  $F_{obs}$  electron density maps showing the electron density in the vicinity of the post-synthetic metalation site in (a) front, (b) side and (c) top views, and (d) an image showing a perspective view of the major occupancy site. The coordination of the Fe consists of two inner-sphere chloride ions, with an outer sphere chloride ion (not shown) for charge compensation. Orange, green, grey, blue, and red spheres represent Fe, Cl, C, N, and O, respectively. H atoms have been omitted for clarity.

Sample	$Fe_3L_3$ ·FeCl <sub>3</sub>	$Mn_{3-x}Fe_x(L_3) \cdot 0.4FeCl_2 (x=0.55)$
Exchange Conditions	FeCl <sub>3</sub> , acetonitrile,	FeCl <sub>2</sub> ·4H <sub>2</sub> O, ethanol,
	60 °C, 5 days	60 °C, 5 days
Crystallographic Parameter		
Formula	$C_{75}H_{66}Cl_{2.8}Fe_4N_{12}O_{14}$	$C_{75}H_{66}Cl_{0.80}Fe_{0.95}Mn_{2.45}N_{12}O_{13.2}$
FW	1682.05	1562.61
Т, К	100(2)	100(2)
Wavelength, Å	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/m$	Monoclinic, $P2_1/m$
Z	2	2
<i>a</i> , Å	12.398 (3)	12.345 (3)
b, Å	33.496 (7)	33.257 (7)
c, Å	12.868 (3)	12.934 (3)
β, °	96.64 (3)	96.66 (3)
<i>V</i> , Å <sup>3</sup>	5308.0 (19)	5274.4 (19)
$d_{\text{calc}}, \text{g/cm}^3$	1.052	0.984
Absorption coefficient, mm <sup>-1</sup>	0.658	0.486
<i>F</i> (000)	1727	1610
Crystal size, mm <sup>3</sup>	$0.20\times0.10\times0.05$	$0.30 \times 0.10 \times 0.05$
Theta range for data collection	1.22 - 27.0	1.66 – 27.0
Index range	$-14 \le h \le 14, -40 \le k \le 40, -15$	$-16 \le h \le 16, -43 \le k \le 43, -16$
	$\leq l \leq 15$	$\leq l \leq 16$
Reflections collected	71745	86249
Independent reflections	9914	11740
Data/restraints/parameters	9914 / 1 / 539	11740 / 0 / 539
GOF on $F^2$	1.301	1.051
Largest diff. peak and hole, $e \cdot A^{-3}$	3.02 and -0.81	1.54 and -1.07
$R_1, [I > 2\sigma(I)]$	0.1077	0.1036
$R_1(wR_2)^a$ , all data	0.1288 (0.3279)	0.1147 (0.2994)
CCDC Number	1443923	1443924

**Table S1.** Crystallographic parameters for the crystal structures of Fe-exchanged  $Mn_3L_3$  samples.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, wR_{2} = \{\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]\}^{1/2}$ 

## References

T. M. McPhillips, S. E. McPhillips, H. J. Chiu, A. E. Cohen, A. M. Deacon, P.
J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis and P.
Kuhn, J. Synchrotron Rad., 2002, 9, 401.

[2] G.M. Sheldrick, Univ. Gottingen, Gottingen, Germany, 2013; Acta Crystallogr., 2008, A64, 112; Acta Crystallogr. 2015, C71, 3.

[3] (a) W. M. Bloch, A. Burgun, C. J. Coghlan, R. Lee, M. L. Coote, C. J. Doonan and C. J. Sumby, *Nat. Chem.*, 2014, 6, 906. (b) W. M. Bloch, A. Burgun, C. J. Doonan and C. J. Sumby, *Chem. Commun.*, 2015, 51, 5486.

[4] (a) A.L. Spek, Acta Crystallogr., 2009, D65, 148; (b) A.L. Spek, Acta
 Crystallogr. 2009, C71, 9.