## ELECTRONIC SUPPLEMENTARY INFORMATION

# Discrete and Encapsulated Molecular Grids: Homometallic Mn<sub>15</sub> and Heterometallic Mn<sub>24</sub>Ni<sub>2</sub> Aggregates

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Fig. S1 Representation of JT axes of the hexacoordinated  $Mn^{III}$  ions (Mn2-Mn6) of each  $Mn^{III}_{6}$ Ni sub-unit present in the molecular structure of 1. Yellow bonds denote JT elongation axes.



**Fig. S2** Plots of the in-phase  $(\chi'_{M})$  (as  $\chi'_{M}T$ ) ac magnetic susceptibility *versus T* for complexes 1.5H<sub>2</sub>O (left) and 2.2py.2H<sub>2</sub>O (right) in a 3.5 G field oscillating at the indicated frequencies and temperature range of 1.8-15 K.



**Fig. S3** Plot of the out-of-phase ( $\chi''_{M}$ ) ac magnetic susceptibility *versus T* for complex 1.5H<sub>2</sub>O in a 3.5 G field oscillating at the indicated frequencies and temperature range of 1.8 - 15 K.



**Fig. S4** Top: Plot of reduced magnetization  $(M/N\mu_B)$  vs H/T for  $2 \cdot 2py \cdot 2H_2O$  at the indicated fields and in the 1.8 - 10 K temperature range. The solid lines are the best fit of the data. Note that the Hamiltonian equation used for the fit of the data is given by eq 1,

$$\mathbf{H} = D\hat{S}_{z}^{2} + g\mu_{\mathrm{B}}\mu_{0}\hat{S}\cdot\boldsymbol{H}$$
<sup>(1)</sup>

where *D* is the axial ZFS parameter,  $\hat{S}_z$  is the easy-axis spin operator,  $\mu_0$  is the vacuum permeability, and *H* is the applied field. The last term in eq 1 is the Zeeman energy associated with an applied magnetic field. See manuscript text for fit details.

Bottom: Plots of reduced magnetization ( $M/N\mu_B$ ) vs H/T for  $2\cdot 2py\cdot 2H_2O$  in the 1.8 – 10 K and 0.1 – 1 T (left) and 0.1 – 7 T (right) ranges.

### Syntheses

All manipulations were performed under aerobic conditions using reagents and solvents as received.  $[Mn_3O(EtCO_2)_6(py)_3](ClO_4)$ ,  $[Mn_3O((CH_3)_3CCO_2)_6(py)_3]$  and  $NBu_4MnO_4$  were prepared as previously described.<sup>1</sup>

 $[Mn_{24}Ni_2O_{30}(EtCO_2)_{16}(MeO)_{12}(MeOH)_8(H_2O)_2]$  (1). Solid NBu<sub>4</sub>MnO<sub>4</sub> (0.01 g, 0.02 mmol) was added to a solution of  $[Mn_3O(EtCO_2)_6(py)_3](ClO_4)$  (0.20 g, 0.21 mmol) and NiCl<sub>2</sub>·6H<sub>2</sub>O (0.15 g, 0.63 mmol) in MeOH (15 mL). The dark red-brown solution was stirred for 3h, then filtered and the filtrate was allowed to stand undisturbed in a closed flask for a period of 2 weeks during which reddish-brown crystals of 1 appeared. The crystals were collected by filtration, washed with MeOH (2x3 mL) and dried under vacuum. Yield, 37% (based on Mn). Vacuum-dried solid analyzed (C, H, N) as 1·5H<sub>2</sub>O. Calcd. (Found): C, 21.27 (21.55); H, 4.25 (4.46) %. Metal analysis was performed via ICP-OES. Calcd. for 1·5H<sub>2</sub>O (found): Mn, 34.34 (34.28); Ni, 3.06 (3.17) %.Selected IR data (KBr, cm<sup>-1</sup>): 3435 (s, br), 2976 (w), 2927 (w), 1578 (m. br), 1190 (w), 1026 (w, br), 606 (s, br).

#### (Me<sub>4</sub>N)<sub>2</sub>[Mn<sub>15</sub>O<sub>10</sub>(OH)<sub>2</sub>(mpt)<sub>4</sub>(hmmbd)<sub>2</sub>((CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>)<sub>8</sub>(py)<sub>2</sub>]·((CH<sub>3</sub>)<sub>3</sub>CCO<sub>2</sub>)<sub>2</sub>H·2py·3.6MeC

**N** (2·2py·3.6MeCN). A solution of H<sub>3</sub>mpt (0.05 g, 0.39 mmol) in MeCN/py (5 mL, 3/1 v/v) was added to a solution of  $[Mn_3O((CH_3)_3CCO_2)_6(py)_3]$  (0.20 g, 0.20 mmol) in MeCN/py (15 mL, 3/1 v/v). Solid Me<sub>4</sub>NOH·5H<sub>2</sub>O (0.07 g, 0.39 mmol) was then added to the reaction mixture and the resulting dark red solution was stirred for 1h. The resulting solution was filtered off and the filtrate allowed to stand undisturbed in a closed flask for a period of ~ 2 weeks during which well-shaped reddish-brown crystals of 2·2py·3.6MeCN were formed. The crystals were collected by filtration, washed with MeCN/py (2x3, 3/1 v/v mL) and dried under vacuum. Yield, 25% (based on Mn). Vacuum-dried solid analyzed (C, H, N) as 2·2py·2H<sub>2</sub>O. Calcd. (Found): C, 41.26 (41.55); H, 6.32 (6.49); N, 2.53 (2.72) %. Selected IR data (KBr, cm<sup>-1</sup>): 2926 (mw), 2912 (mw), 2857 (w), 1543 (s), 1475 (sm), 1406 (sm), 1358 (sm), 1213 (s), 1119 (s), 1069 (s), 928 (sm), 866 (sm), 694 (s), 608 (mw), 553 (sm).

	Mn(II)	Mn(III)	Mn(IV)	Ni(II)
Mn1	3.10	<u>2.84</u>	2.98	2.40
Mn2	3.28	<u>3.00</u>	3.15	2.54
Mn3	3.26	<u>2.98</u>	3.13	2.52
Mn4	3.24	<u>2.97</u>	3.12	2.51
Mn5	3.23	<u>2.96</u>	3.11	2.50
Mn6	3.16	<u>2.89</u>	3.03	2.44
Mn7	4.13	3.77	<u>3.96</u>	3.19
Mn8	4.24	3.88	<u>4.07</u>	3.28
Mn9	4.18	3.83	<u>4.02</u>	3.24
Mn10	4.15	3.90	<u>3.99</u>	3.21
Mn11	4.08	3.73	<u>3.92</u>	3.16
Mn12	4.15	3.80	<u>3.99</u>	3.21
Ni1	2.78	2.55	2.67	<u>2.15</u>

Table S1. Bond Valence Sums for the Mn and Ni atoms in complex 1.<sup>a</sup>

<sup>*a*</sup> The underlined value is the one closest to the charge for which it was calculated.

	Mn(II)	Mn(III)	Mn(IV)
Mn1	3.21	2.93	3.08
Mn2	4.14	3.78	<u>3.97</u>
Mn3	3.25	<u>2.97</u>	3.12
Mn4	3.17	<u>2.92</u>	3.04
Mn5	3.26	<u>2.98</u>	3.13
Mn6	3.28	<u>3.20</u>	3.29
Mn7	3.17	<u>2.92</u>	3.04
Mn8	3.26	<u>3.01</u>	3.12

Table S2. Bond Valence Sums for the Mn atoms in complex 2.2py-3.6MeCN.<sup>a</sup>

<sup>*a*</sup> The underlined value is the one closest to the charge for which it was calculated.

1			<b>2</b> ·2py·3.6MeCN		
	BVS	Protonation level		BVS	Protonation level
01	1.947	O <sup>2-</sup>	018	1.749	O <sup>2-</sup>
02	1.983	O <sup>2-</sup>	019	1.773	O <sup>2-</sup>
03	2.017	O <sup>2-</sup>	O20	1.739	O <sup>2-</sup>
04	1.972	O <sup>2-</sup>	O21	1.674	O <sup>2-</sup>
05	1.624	O <sup>2-</sup>	022	1.843	O <sup>2-</sup>
O6	1.897	O <sup>2-</sup>	023	1.098	OH-
07	1.981	O <sup>2-</sup>			
08	1.898	O <sup>2-</sup>			
09	1.903	O <sup>2-</sup>			
O10	2.019	O <sup>2-</sup>			
011	1.855	O <sup>2-</sup>			
012	1.720	O <sup>2-</sup>			
013	1.955	O <sup>2-</sup>			
014	1.713	O <sup>2-</sup>			
015	1.893	O <sup>2-</sup>			

Table S3. Bond Valence Sums for the O atoms in complexes 1 and 2.2py-3.6MeCN.

#### References

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