

Supplementary Materials (SM) for:

Selective formation, reactivity, redox and magnetic properties of Mn^{III} and Fe^{III} dinuclear complexes with shortened salen-type Schiff base ligands

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Experimental section (cont.)

Synthesis of [Mn₂(μ-salmen)₂(μ-OMe)₂] (3b)

This dark green compound was prepared as **3a** starting from Mn(AcO)₃·2H₂O (211.2 mg, 0.79 mmol), H₂salmen (200.1 mg, 0.79 mmol), Et₃N (3 mL) and MeOH (15 mL). Yield: 219.7 mg (80%). Anal (%) calcd for C₃₂H₃₀Mn₂N₄O₆·2H₂O (694.54): C 55.34, H 4.35, N 8.10. Found: C 55.40, H 4.72, N 7.96. ESI-MS (MeOH): *m/z* 645 ([M – OMe]⁺, 100%). IR (KBr): ν_{max}/cm⁻¹ 1631 (C=N).

Synthesis of [Mn₂(μ-salmen)₂(μ-OH)₂] (3c)

This dark green compound was prepared as **3a** starting from Mn(AcO)₃·2H₂O (49.1 mg, 0.20 mmol), H₂salmen (50.2 mg, 0.20 mmol), Et₃N (3 mL) and *i*PrOH (15 mL). Yield: 73.9 mg (60%). Anal (%) calcd for C₃₀H₂₆Mn₂N₄O₆·5H₂O (738.50): C 48.79, H 4.91, N 7.59. Found: C 48.94, H 4.64, N 7.52. IR (KBr): ν_{max}/cm⁻¹ 1625 (C=N).

Synthesis of [Fe₂(μ-salmen)₂(μ-OMe)₂] (4b)

This dark brown compound was prepared as **4a** starting from FeCl₃ (128.2 mg, 0.79 mmol), H₂salmen (201.0 mg, 0.79 mmol), Et₃N (3 mL) and MeOH (15 mL). Yield: 209.2 mg (78%). Anal (%) calcd for C₃₂H₃₀Fe₂N₄O₆ (678.34): C 56.66, H 4.46, N 8.26. Found: C 56.33, H 4.73, N 8.13. ESI-MS (MeOH): *m/z* 647 ([M – OMe]⁺, 60%), 701 ([M + Na]⁺, 100). IR (KBr): ν_{max}/cm⁻¹ 1616 (C=N).

Synthesis of [Fe₂(μ-salmen)₂(μ-OH)₂] (4c)

This dark green compound was prepared as **4a** starting from FeCl₃ (32.0 mg, 0.20 mmol), H₂salmen (50.2 mg, 0.20 mmol), Et₃N (3 mL) and *i*PrOH (15 mL). Yield: 46.7 mg (70%). Anal (%) calcd for C₃₀H₂₆Fe₂N₄O₆·H₂O (668.30): C 53.92, H 4.22, N 8.38. Found: C 53.55, H 4.06, N 8.14. ESI-MS (MeOH): *m/z* 633 ([M – OH]⁺, 10%), 647 ([M – 2OH + OMe]⁺, 100) (OH/OMe exchange in MeOH solution). IR (KBr): ν_{max}/cm⁻¹ 1613 (C=N).

Synthesis of [Mn₂(μ-sal(*p*-Me)ben)₂(μ-OMe)₂] (5b)

This compound was prepared as **5a** starting from Mn(AcO)₃·2H₂O (76.5 mg, 0.44 mmol) and H₂sal(*p*-Me)ben (152.0 mg, 0.44 mmol). Yield: 84.8 mg (45%). Anal (%) calcd for C₄₆H₄₂Mn₂N₄O₆ (856.74): C 64.50, H 4.94, N 6.54. Found: C 64.87, H 4.80, N 6.54. ESI-MS (MeOH): *m/z* 825 ([M – OMe]⁺, 100%), 879 ([M + Na]⁺, 50). IR (KBr): ν_{max}/cm⁻¹ 1621 (C=N).

Synthesis of [Mn₂(μ-salben)₂(μ-OMe)₂] (5c)

This compound was prepared as **5a** starting from Mn(AcO)₃·2H₂O (117.3 mg, 0.68 mmol) and H₂salben (220.2 mg, 0.67 mmol). Yield: 104.3 mg (38%). Anal (%) calcd for C₄₄H₃₈Mn₂N₄O₆ (828.69): C 63.77, H 4.62, N 6.76. Found: C 63.76, H 4.86, N 6.77. ESI-MS (MeOH): *m/z* 797 ([M – OMe]⁺, 100%), 851 ([M + Na]⁺, 40). IR (KBr): ν_{max}/cm⁻¹ 1622 (C=N).

Synthesis of [Mn₂(μ-sal(*p*-F)ben)₂(μ-OMe)₂] (5d)

This compound was prepared as **5a** starting from Mn(AcO)₃·2H₂O (77.5 mg, 0.45 mmol) and H₂sal(*p*-F)ben (153.1 mg, 0.44 mmol). Yield: 62.8 mg (33%). Anal (%) calcd for C₄₄H₃₆F₂Mn₂N₄O₆ (864.67): C 61.12, H 4.20, N 6.48. Found: C 60.75, H 4.30, N 6.41. ESI-MS (MeOH): not soluble. IR (KBr): ν_{max}/cm⁻¹ 1622 (C=N).

Synthesis of [Mn₂(μ-sal(*p*-Cl)ben)₂(μ-OMe)₂] (5e)

This compound was prepared as **5a** starting from Mn(AcO)₃·2H₂O (169.5 mg, 0.97 mmol) and H₂sal(*p*-Cl)ben (355.5 mg, 0.99 mmol). Yield: 189.8 mg (43%). Anal (%) calcd for C₄₄H₃₆Cl₂Mn₂N₄O₆·H₂O (915.59): C 57.72, H 4.18, N 6.12. Found: C 57.55, H 4.23, N 6.04. ESI-MS (MeOH): *m/z* 865 ([M – OMe]⁺, 100%), 897 ([M + H]⁺, 95), 919 ([M + Na]⁺, 10). IR (KBr): ν_{max}/cm⁻¹ 1620 (C=N).

Synthesis of [Mn₂(μ-sal(*p*-CF₃)ben)₂(μ-OMe)₂] (5f)

This compound was prepared as **5a** starting from Mn(AcO)₃·2H₂O (69.1 mg, 0.40 mmol) and H₂sal(*p*-CF₃)ben (152.6 mg, 0.38 mmol). Yield: 86.5 mg (47%). Anal (%) calcd for C₄₆H₃₆F₆Mn₂N₄O₆ (964.68): C 57.27, H 3.76, N 5.81. Found: C 57.34, H 3.64, N 5.73. ESI-MS (MeOH): not soluble. IR (KBr): ν_{max}/cm⁻¹ 1621 (C=N).

Synthesis of [Mn₂(μ-sal(*p*-NO₂)ben)₂(μ-OMe)₂] (5g)

This compound was prepared as **5a** starting from Mn(AcO)₃·2H₂O (34.0 mg, 0.13 mmol) and H₂sal(*p*-NO₂)ben (50.0 mg, 0.13 mmol). Yield: 57.3 mg (53%). Anal (%) calcd for C₄₄H₃₆Mn₂N₆O₁₀·MeOH (964.68): C 56.85, H 4.24, N 8.84. Found: C 56.41, H 3.92, N 8.82. ESI-MS (MeOH): not soluble. IR (KBr): ν_{max}/cm⁻¹ 1619 (C=N).

Synthesis of [Fe₂(μ-sal(*p*-Me)ben)₂(μ-OMe)₂] (6b)

The synthesis of this compound was performed as **6a** different times starting from Fe(NO₃)₃·9H₂O or FeCl₃ and H₂sal(*p*-Me)ben in equimolar ratio, but little solid was left after mixing all times, and precipitation of the reaction solution with H₂O or *i*Pr₂O always yielded a red solid, whose IR spectrum invariably presented the N–H stretching of the hydrolysed sal(*p*-Me)ben²⁻ ligand to salim⁻ at 3305 cm⁻¹, together with the C=O stretching of the free *para*-methylbenzaldehyde at 1700 cm⁻¹. The C=N stretching at 1617 cm⁻¹ is also present.

Synthesis of [Fe₂(μ-salben)₂(μ-OMe)₂] (6c)

This compound was prepared as **6a** starting from Fe(NO₃)₃·9H₂O (124.4 mg, 0.308 mmol) and H₂salben (101.9 mg, 0.308 mmol). Yield: 73.3 mg (54%). Anal (%) calcd for C₄₄H₃₈Fe₂N₄O₆·MeOH·H₂O (880.557): C 61.38, H 5.04, N 6.36. Found: C 61.32, H 4.66, N 6.36. IR (KBr): ν_{max}/cm⁻¹ 1614 (C=N). ESI-MS (MeOH): *m/z* 799 ([M – OMe]⁺, 100%), 853 ([M + Na]⁺, 30), 881 ([M + MeOH + H₂O + H]⁺, 40). **Warning!** The reaction mixture was left under stirring only 1 h at room temperature and then the title compound was isolated as dark red solid by filtration. For longer times, as for **6b**, the solid slowly disappeared leaving a red solution; the addition of water led to the precipitation of a brown-red solid, which revealed the presence of one hydrolysed salben²⁻ ligand to two salim⁻, as evidenced in the infrared spectrum by the N–H stretching at 3302 cm⁻¹ and the C=O stretching of the free benzaldehyde at 1697. The C=N stretching at 1616 cm⁻¹ is also present. ESI-MS (MeOH): *m/z* 606 ([Fe₂(salmp)(salim)(OMe)]⁺, 100%), 749 ([Fe₂(salmp)(salim)₂(OMe) + Na]⁺, 50).

Synthesis of [Fe₂(μ-sal(*p*-F)ben)₂(μ-OMe)₂] (6d)

The synthesis of this compound was performed as **6a** different times starting from Fe(NO₃)₃·9H₂O or FeCl₃ and H₂sal(*p*-F)ben, but in all cases little solid was left after mixing for 1 h, and

precipitation of the reaction solution with H₂O or *i*Pr₂O always yielded a red solid whose IR spectrum invariably presented the N–H stretching of the hydrolysed sal(*p*-F)ben²⁻ ligand to salim⁻ at 3313 cm⁻¹, together with the C=O stretching of the free *p*-F-benzaldehyde at 1690 cm⁻¹. The C=N stretching at 1615 cm⁻¹ is also present. ESI-MS (MeOH): *m/z* 606 ([Fe₂(salmp)(salim)(OMe)]⁺, 100%), 749 ([Fe₂(salmp)(salim)₂(OMe) + Na]⁺, 10), 883 ([Fe₂(salmp)(salim)₂(OMe) + *p*-F-benzaldehyde·MeOH + H]⁺, 60), where *p*-F-benzaldehyde·MeOH = hemiacetal.

Synthesis of [Fe₂(μ-sal(*p*-Cl)ben)₂(μ-OMe)₂] (6e)

This compound was prepared as **6a** starting from Fe(NO₃)₃·9H₂O (357.4 mg, 0.885 mmol) and H₂sal(*p*-Cl)ben (315.3 mg, 0.864 mmol). Yield: 156.1 mg (34%). Anal (%) calcd for C₄₄H₃₆Cl₂Fe₂N₄O₆·2MeOH·H₂O (981.49): C 56.29, H 4.72, N 5.71. Found: C 56.68, H 4.37, N 5.72. IR (KBr): ν_{max}/cm⁻¹ 1614 (C=N). ESI-MS (MeOH) on freshly-prepared solution: *m/z* 867 ([M – OMe]⁺, 100%), 899 ([M + 1]⁺, 20), 921 ([M + Na]⁺, 45). ESI-MS (MeOH) on aged solution for 1 day: *m/z* 656 ([Fe₂(sal(*p*-Cl)ben)(salim)(OMe)₂]⁺, 25%), 799 ([Fe₂(sal(*p*-Cl)ben)(salim)₂(OMe)₂ + Na]⁺, 100), 867 ([M – OMe]⁺, 10), 899 ([M + 1]⁺, 20), 921 ([M + Na]⁺, 10).

Synthesis of [Fe₂(μ-sal(*p*-CF₃)ben)₂(μ-OMe)₂] (6f)

The synthesis of this compound was performed as **6a** different times starting from Fe(NO₃)₃·9H₂O or FeCl₃ and H₂sal(*p*-CF₃)ben, but in all cases little solid was left after mixing for 1 h, and precipitation of the reaction solution with H₂O or *i*Pr₂O always yielded a red solid, whose IR spectrum invariably presented the N–H stretching of the hydrolysed sal(*p*-CF₃)ben²⁻ ligand to salim⁻ at 3296 cm⁻¹, together with the C=O stretching of the free *p*-CF₃-salicylaldehyde at about 1700⁻¹. The C=N stretching at 1616 cm⁻¹ is also present.

Synthesis of [Fe₂(μ-sal(*p*-NO₂)ben)₂(μ-OMe)₂] (6g)

The synthesis of this compound was performed as **6a** different times starting from Fe(NO₃)₃·9H₂O or FeCl₃ and H₂sal(*p*-NO₂)ben, but in all cases little solid was left after mixing, and precipitation of the reaction mixture with H₂O or *i*Pr₂O always yielded a solid, whose IR spectrum invariably presented the N–H stretching of the hydrolysed sal(*p*-NO₂)ben²⁻ ligand to salim⁻ at 3316 cm⁻¹, together with the C=O stretching of the free *p*-NO₂-salicylaldehyde at 1724 cm⁻¹. The C=N stretching at 1616 cm⁻¹ is also present.

Table S1. Crystallographic data for H₂sal(*p*-*t*Bu)ben, H₂sal(*p*-CF₃)ben, **2a**·2AcOEt, **2a**·2CH₃CN, **2b**·1.5H₂O and **3c**·2DMF.

	H ₂ sal(<i>p</i> - <i>t</i> Bu)ben	H ₂ sal(<i>p</i> -CF ₃)ben	2a ·2AcOEt
<i>Crystal Data</i>			
Moiety formula	C ₂₅ H ₁₇ N ₂ O ₂	C ₂₂ H ₁₇ F ₃ N ₂ O ₂	C ₄₂ H ₃₀ Fe ₂ N ₄ O ₆ ·2C ₄ H ₈ O ₂
<i>M</i>	377.40	398.37	974.61
Crystal system	orthorhombic	orthorhombic	triclinic
Space group	<i>Pnma</i> (n. 62)	<i>Pna2₁</i> (n. 33)	<i>P</i> −1 (n. 2)
<i>a</i> / Å	11.0752(16)	9.806(2)	9.914(2)
<i>b</i> / Å	19.832(3)	14.949(3)	10.524(2)
<i>c</i> / Å	9.9100(15)	13.214(3)	10.892(2)
α / °	90	90	92.53(3)
β / °	90	90	100.72(3)
γ / °	90	90	90.38(3)
<i>V</i> / Å ³	2176.7(6)	1937.0(7)	1115.4(4)
<i>Z</i>	4	4	1
ρ_{calc} / g cm ^{−3}	1.152	1.366	1.451
μ / mm ^{−1}	0.063	0.108	0.716
Colour, habit	colourless, prism	colourless, prism	brown, pseudoprism
Dimensions / mm	0.25 × 0.15 × 0.08	0.25 × 0.10 × 0.03	0.12 × 0.08 × 0.05
<i>Data Collection</i>			
Temperature / K	292(2)	294(2)	294(2)
radiation λ / Å	Mo K α , 0.71073	Mo K α , 0.71073	Mo K α , 0.71073
$2\theta_{\text{max}}$ / °	52.9	36.5	57.9
Measured reflections	14942	5048	8669
Independent reflections	2314	1386	5143
Reflections [<i>I</i> > 2 σ (<i>I</i>)]	1473	1303	3583
<i>R</i> _{int}	0.038	0.021	0.030
<i>Data refinement</i>			
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0605, 0.1890	0.0315, 0.0821	0.0474, 0.1144
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0860, 0.2144	0.0344, 0.0848	0.0867, 0.1381
Goodness of fit <i>S</i>	0.965	1.045	1.045
Flack parameter	–	0.2(4)	–
Parameters, restraints	158, 0	270, 1	298, 0
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ / e Å ^{−3}	0.27, −0.17	0.17, −0.11	0.60, −0.57

Table S1 (cont.)

	2a ·2CH ₃ CN	2b ·1.5H ₂ O	3c ·2DMF
<i>Crystal Data</i>			
Moiety formula	C ₄₂ H ₃₀ Fe ₂ N ₄ O ₆ ·2C ₂ H ₃ N	C ₃₆ H ₃₀ Fe ₂ N ₄ O ₆ ·1.5H ₂ O	C ₃₀ H ₂₆ Mn ₂ N ₄ O ₆ ·2C ₃ H ₇ NO
<i>M</i>	880.51	753.36	794.62
Crystal system	triclinic	orthorhombic	triclinic
Space group	<i>P</i> −1 (n. 2)	<i>Pmc</i> 2 ₁ (n. 26)	<i>P</i> −1 (n. 2)
<i>a</i> / Å	9.807(2)	17.4994(18)	9.7228(14)
<i>b</i> / Å	10.787(2)	10.5522(11)	9.8409(14)
<i>c</i> / Å	11.396(2)	18.5062(19)	10.8652(16)
α / °	70.17(3)	90	65.480(10)
β / °	65.23(3)	90	67.880(10)
γ / °	88.98(3)	90	83.170(10)
<i>V</i> / Å ³	1018.8(5)	3417.3(6)	875.4(2)
<i>Z</i>	1	4	1
ρ_{calc} / g cm ^{−3}	1.435	1.464	1.507
μ / mm ^{−1}	0.770	0.906	0.783
Colour, habit	brown, prism	brown, prism	brown, pseudoprism
Dimensions / mm	0.15 × 0.10 × 0.08	0.15 × 0.06 × 0.05	0.15 × 0.07 × 0.05
<i>Data Collection</i>			
Temperature / K	293(2)	294(2)	294(2)
radiation λ / Å	Mo K α , 0.71073	Mo K α , 0.71073	Mo K α , 0.71073
$2\theta_{\text{max}}$ / °	46.2	57.4	58.3
Measured reflections	5328	27448	8175
Independent reflections	2851	8855	4337
Reflections [$I > 2\sigma(I)$]	2415	5677	3262
<i>R</i> _{int}	0.020	0.049	0.096
<i>Data refinement</i>			
<i>R</i> ₁ , <i>wR</i> ₂ [$I > 2\sigma(I)$]	0.0294, 0.0678	0.0400, 0.0898	0.0333, 0.0860
<i>R</i> ₁ , <i>wR</i> ₂ [all data]	0.0364, 0.0705	0.0771, 0.1031	0.0587, 0.1033
Goodness of fit <i>S</i>	0.981	0.947	1.087
Flack parameter	–	−0.009(8)	–
Parameters, restraints	271, 0	487, 1	247, 0
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ / e Å ^{−3}	0.18, −0.22	0.42, −0.29	0.41, −0.64

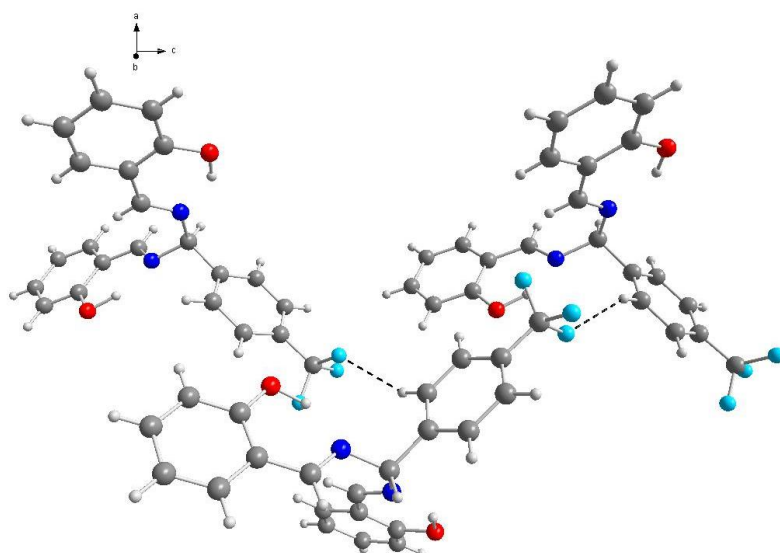
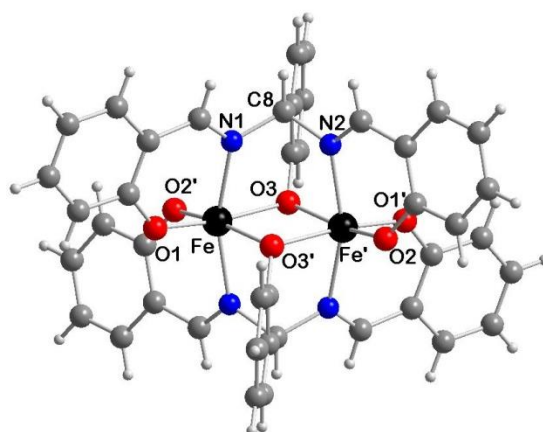
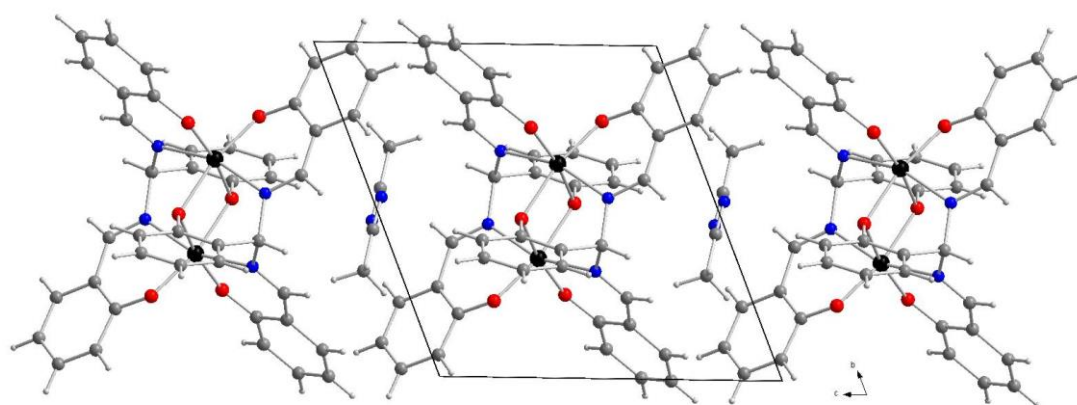


Figure S1. Intermolecular hydrogen bonds in $\text{H}_2\text{sal}(p\text{-CF}_3)\text{ben}$. Colour code: O = red, N = blue, C = grey, H = white, F = turquoise.



(a)



(b)

Figure S2. (a) Crystal structure of $2\mathbf{a} \cdot 2\text{CH}_3\text{CN}$ with main atom numbering and (b) its crystal packing; colour code: Fe = black, O = red, N = blue, C = grey, H = white.

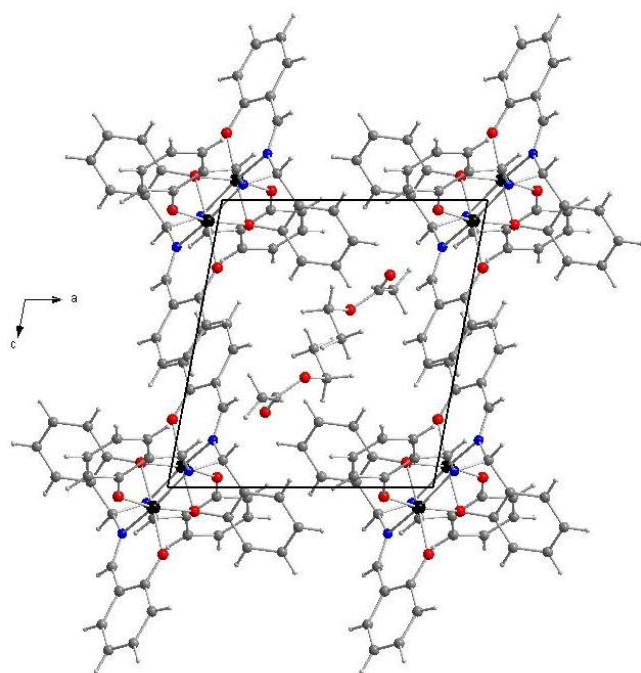


Figure S3. Crystal packing of **2a·2AcOEt**; colour code: Fe = black, O = red, N = blue, C = grey, H = white.

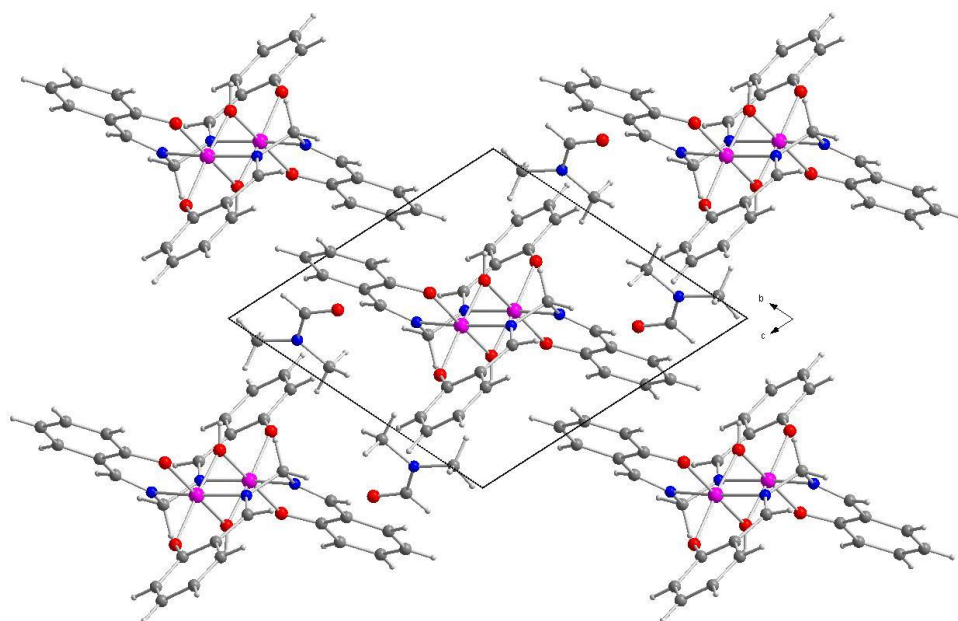


Figure S4. Crystal packing of **3c·2DMF**; colour code: Mn = violet, O = red, N = blue, C = grey, H = white.

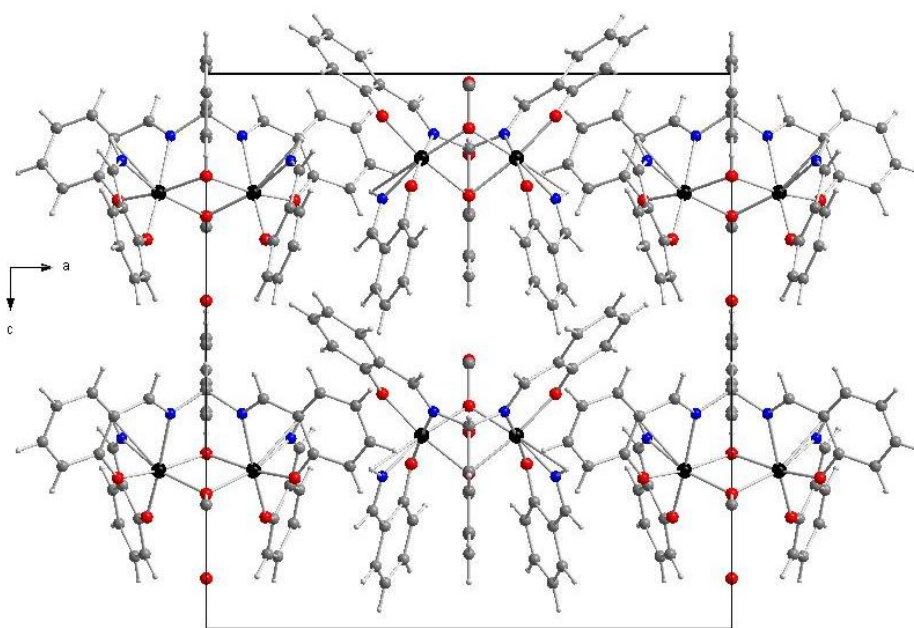


Figure S5. Crystal packing of **2b**·1.5H₂O; colour code: Fe = black, O = red, N = blue, C = grey, H = white.

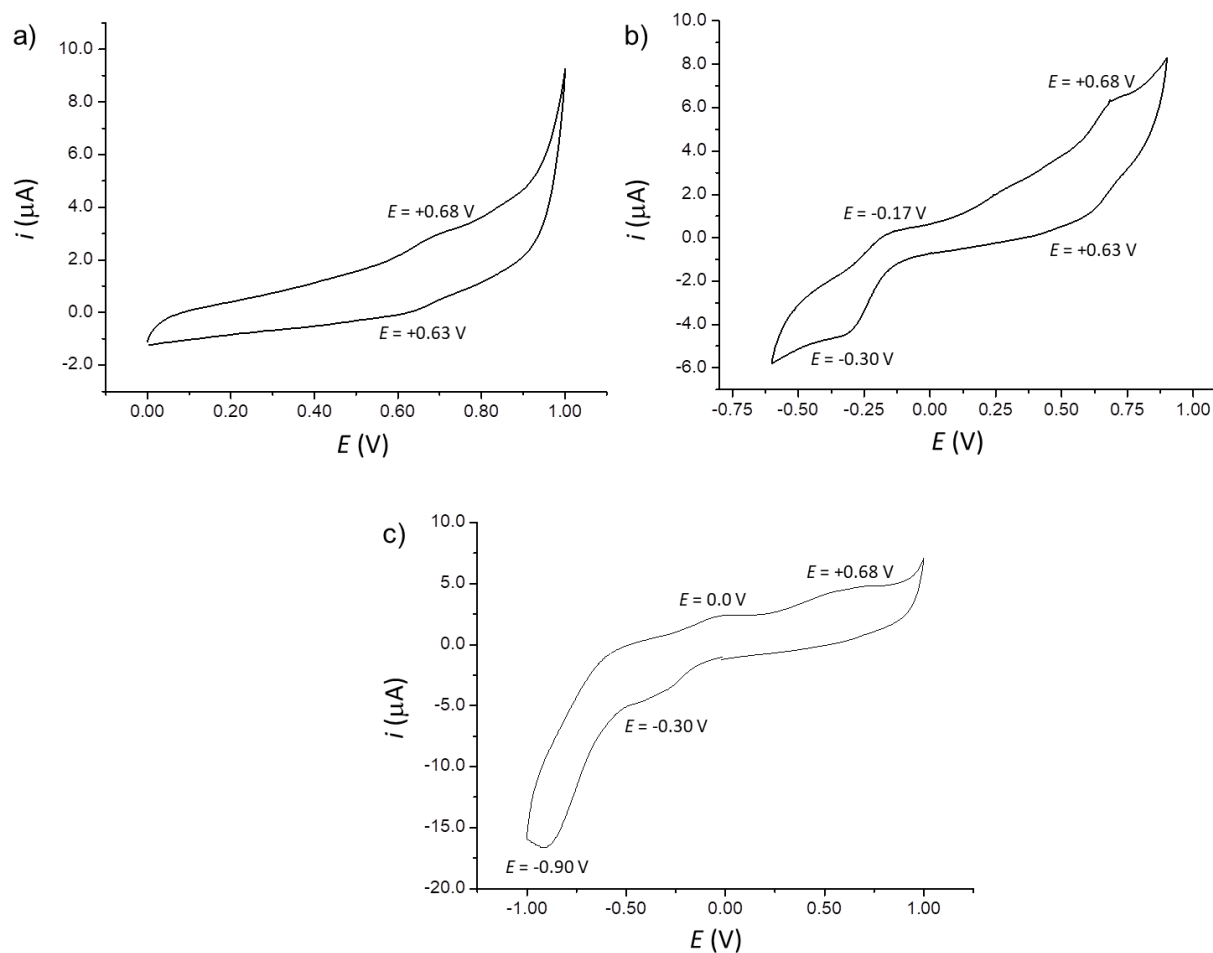


Figure S6. CV scans of **3b** recorded in DMF 0.1 M TBAPF₆ at 50 mV/s scan rate; potentials measured *vs* Ag/AgCl, 3 M KCl reference electrode.

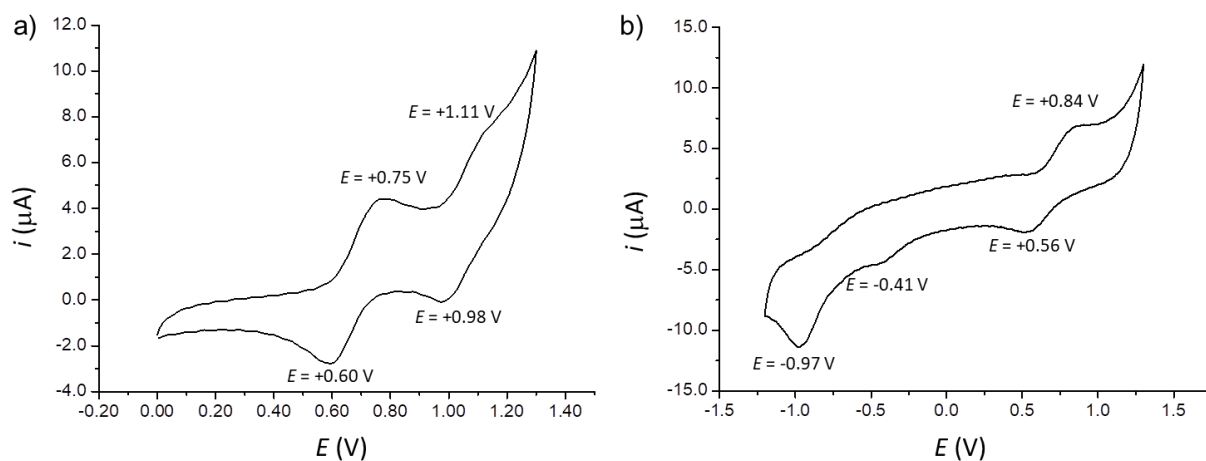


Figure S7. CV scans of **5a** recorded in DMF 0.1 M TBAPF₆ at 50 mV/s scan rate; potentials measured *vs* Ag/AgCl, 3 M KCl reference electrode.

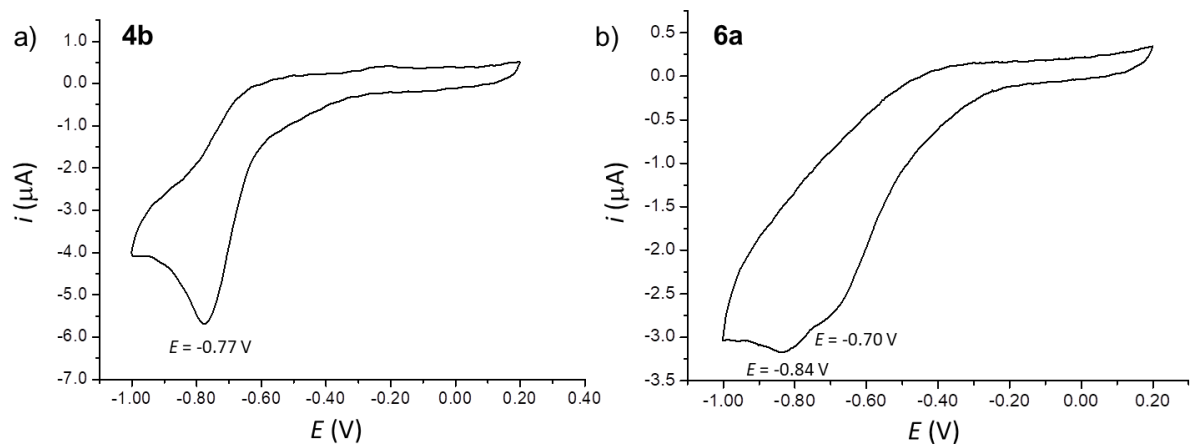


Figure S8. CV scans of a) **4b** and b) **6a** recorded in DMF 0.1 M TBAPF₆ at 50 mV/s scan rate; potentials measured *vs* Ag/AgCl, 3 M KCl reference electrode.

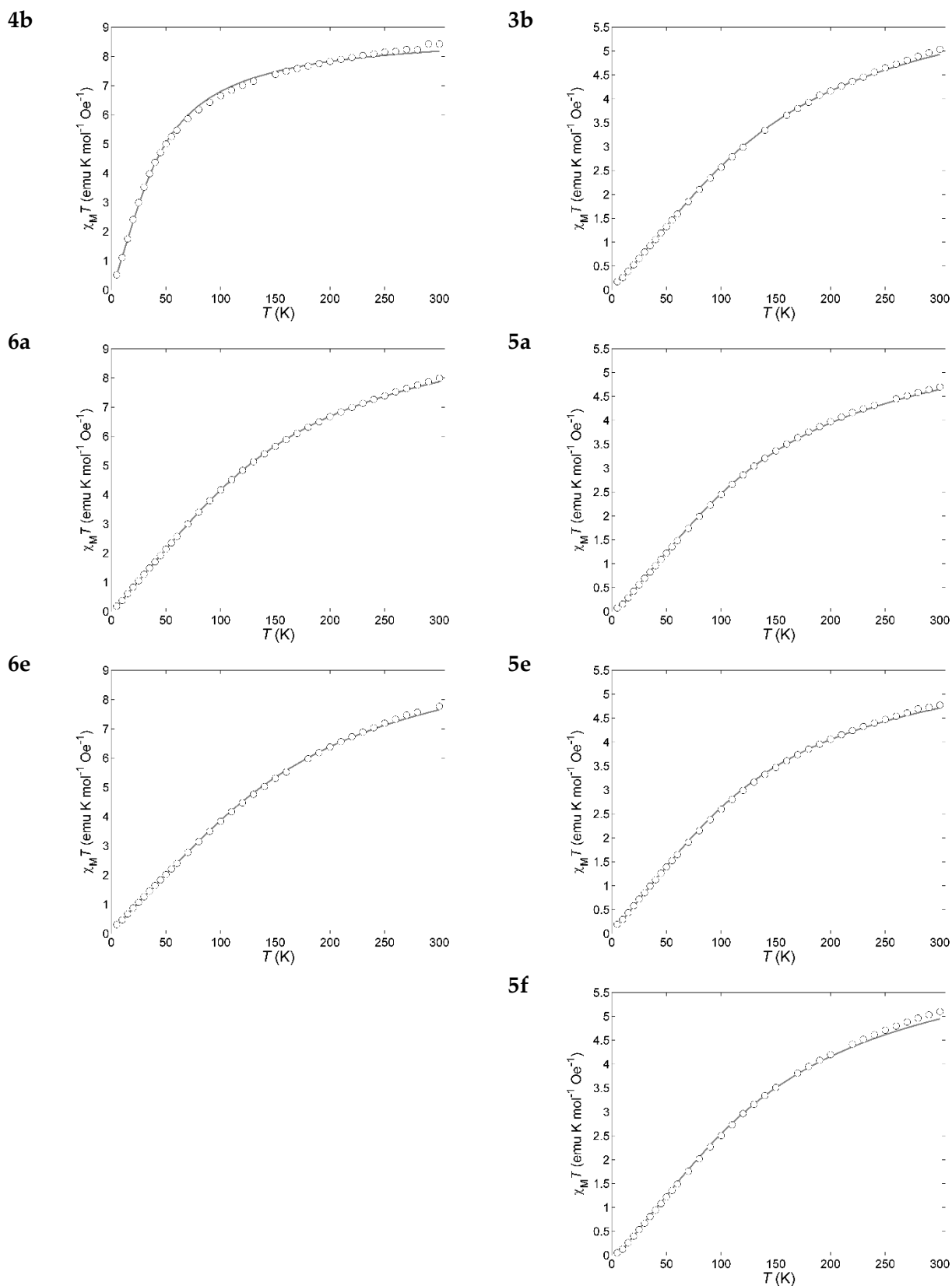


Figure S7. Temperature dependence of the molar susceptibility of iron(III) (**4b**, **6a**, **6e**) and manganese(III) (**3b**, **5a**, **5e**, **5f**) dinuclear compounds.