Supporting information

Molecular self-assemblies of a π-conjugated redox-active bipyridinium cation with magnetic dimetallic oxalate-bridged trimeric clusters

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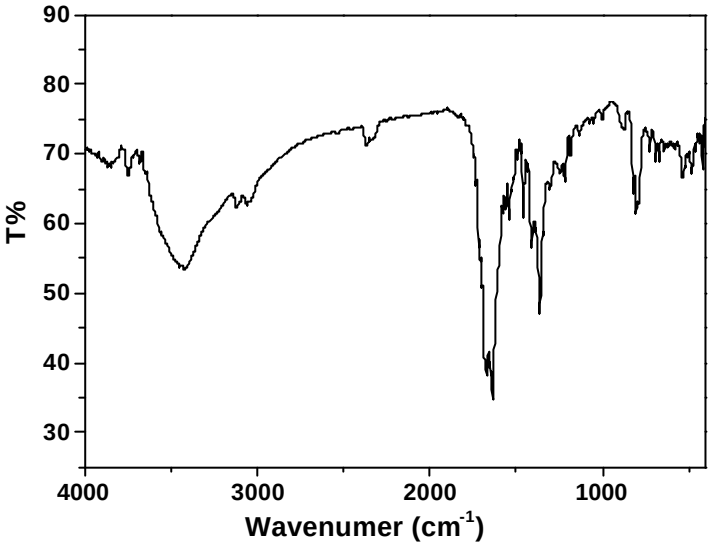


Fig. 1S IR spectrum of compound **1 $(Bpyph)_2\{Mn^{II}(H_2O)_2[Fe^{III}(C_2O_4)_3]_2\}\cdot 12.5H_2O$**

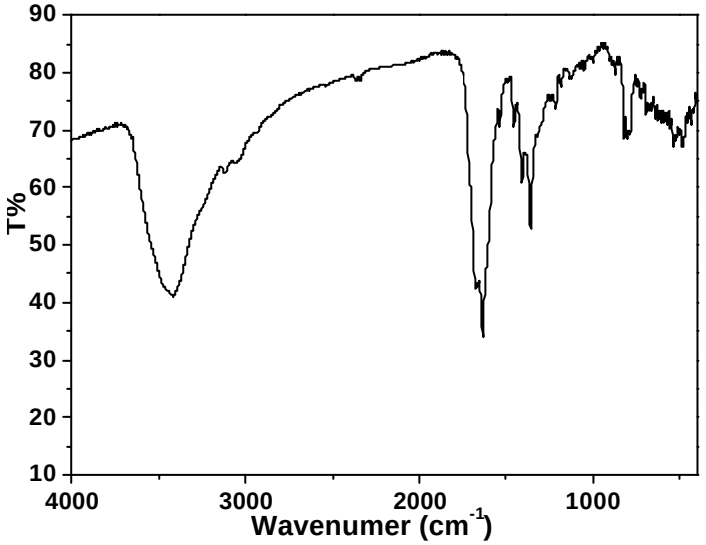


Fig. 2S IR spectrum of compound **2, $(Bpyph)_2\{Co^{II}(H_2O)_2[Fe^{III}(C_2O_4)_3]_2\}\cdot 12.5H_2O$**

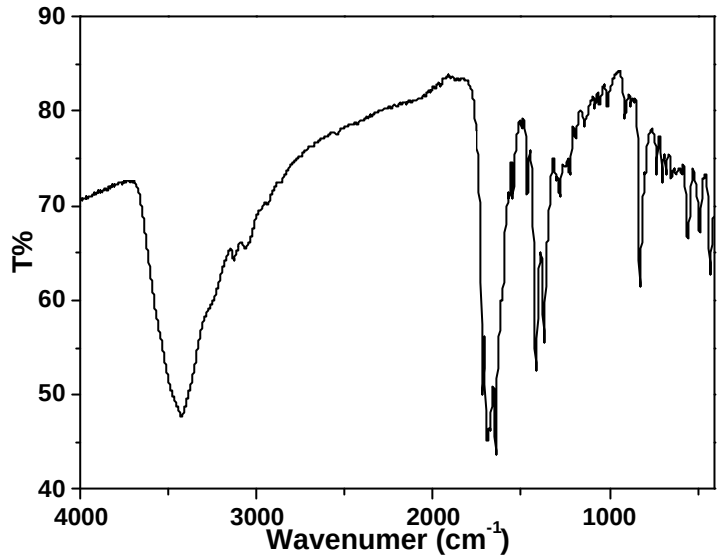


Fig. 3S IR spectrum of compound **3, $(Bpyph)_2\{Mn^{II}(H_2O)_2[Cr^{III}(C_2O_4)_3]_2\}\cdot 12.5H_2O$**

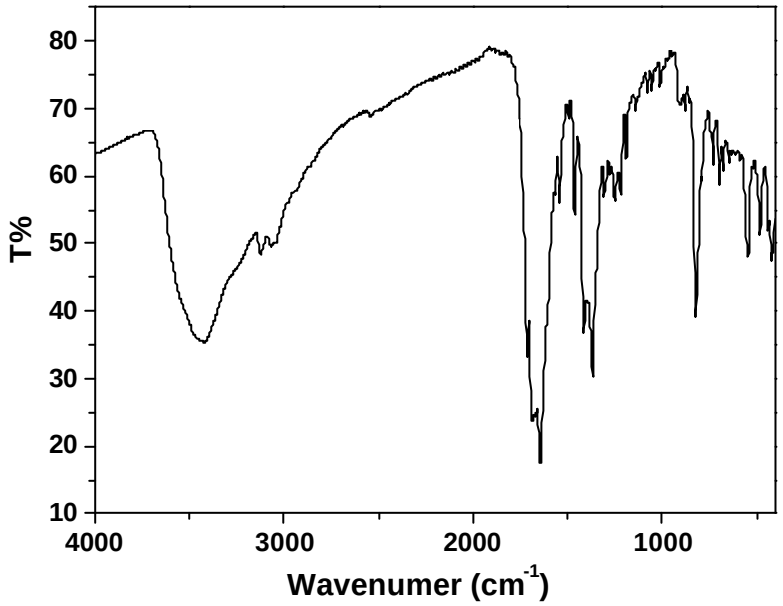


Fig. 4S IR spectrum of compound **4, $(Bpyph)_2\{Co^{II}(H_2O)_2[Cr^{III}(C_2O_4)_3]_2\}\cdot 12.5H_2O$**

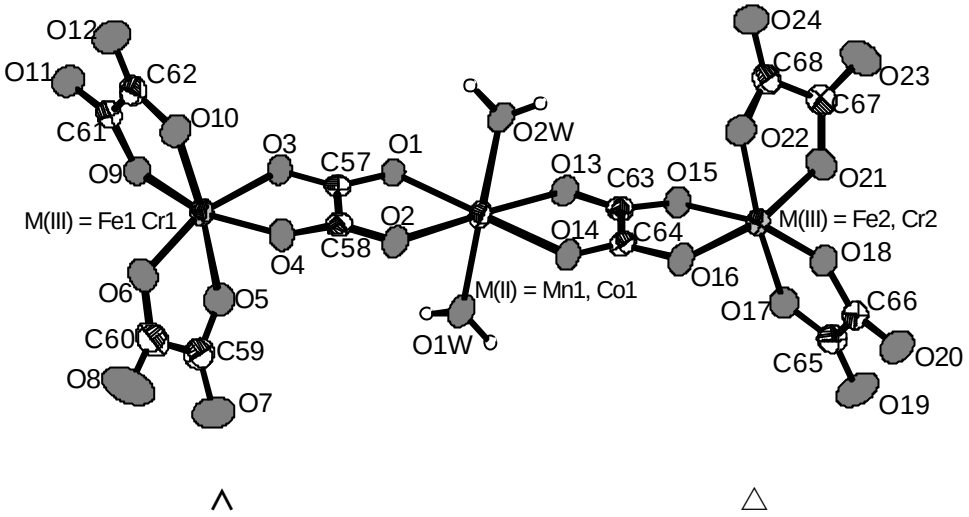
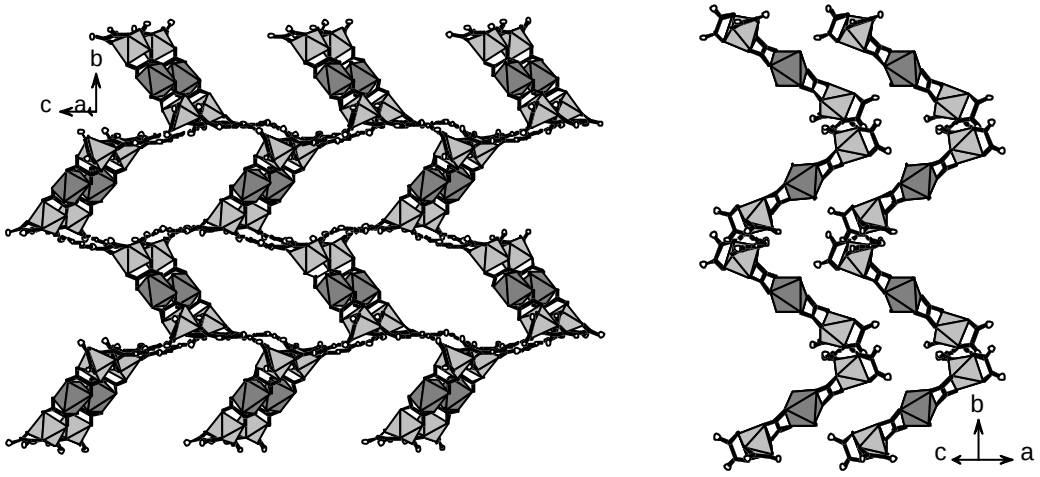
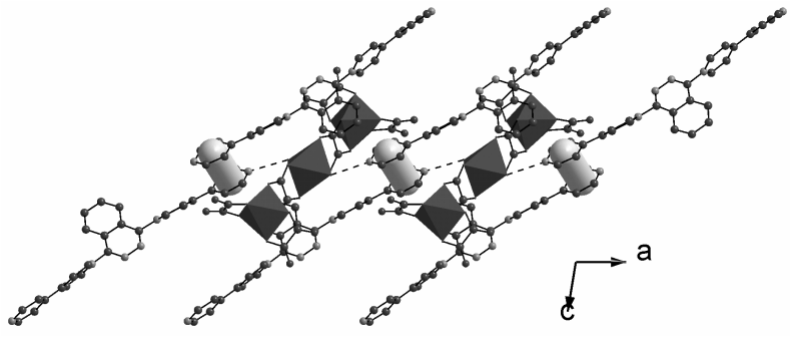


Fig. 5S Different chirality of the $[Fe(ox)_3]^{3-}$ unit in compound **1**, **$(Bpyph)_2\{Mn^{II}(H_2O)_2[Fe^{III}(C_2O_4)_3]_2\}\cdot 12.5H_2O$**

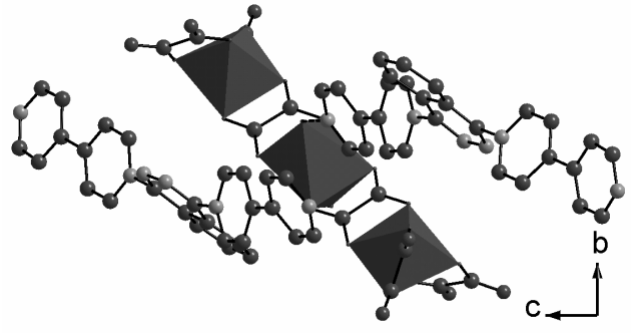


(a) **(b)**

Fig. 6S Stacking structure of 2-D hydrogen bonding network in compound **1** (a) viewed close to *a*- axis, (b) viewed along [101] direction.

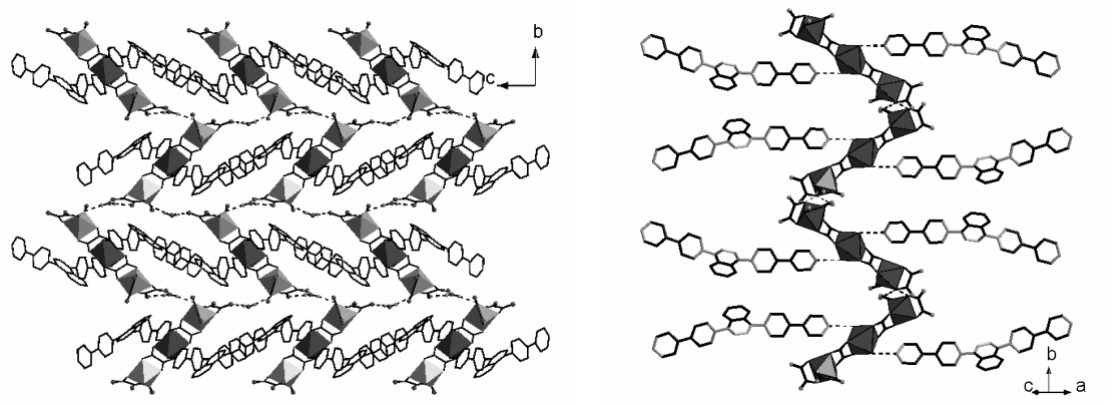


(a)



(b)

Fig. 7S View of the infinite ribbons built from alternating $Bpyph^{2+}$ cations and dimetallic trimers through hydrogen bonding and π-π stacking interactions along *b*-axis (a) and *a*-axis (b) direction. All H atoms are omitted for clarity. The black dashed lines denote hydrogen bonds, and the light grey shadows in (a) represent π–π interactions.



(a) (b)

Fig. 8S A perspective view of 2-D hydrogen bonded metal-oxalate network with $BPyph^{2+}$ cations attached. (a) viewed along *a*-axis, (b) viewed along [101] direction.

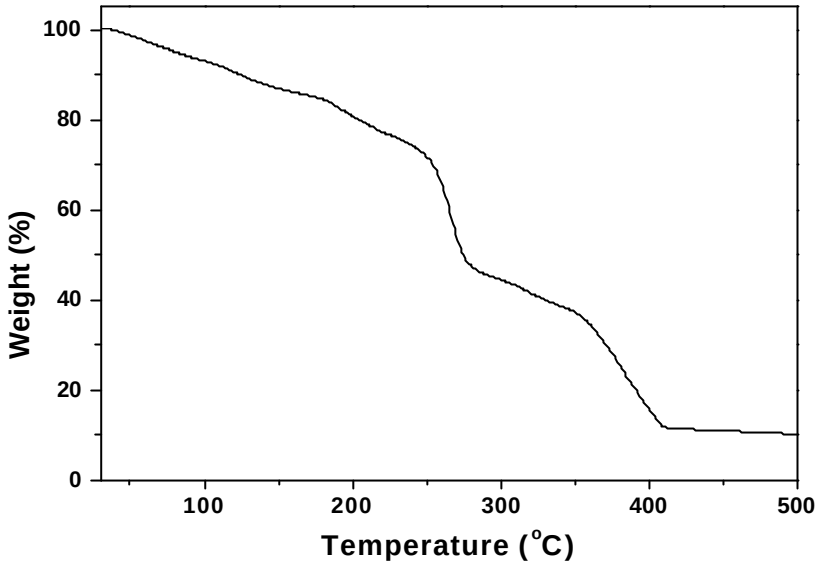


Fig. 9S The TGA plot for compound **1**, **$(Bpyph)_2\{Mn(H_2O)_2[Fe(C_2O_4)_3]_2\}\cdot 12.5H_2O$**

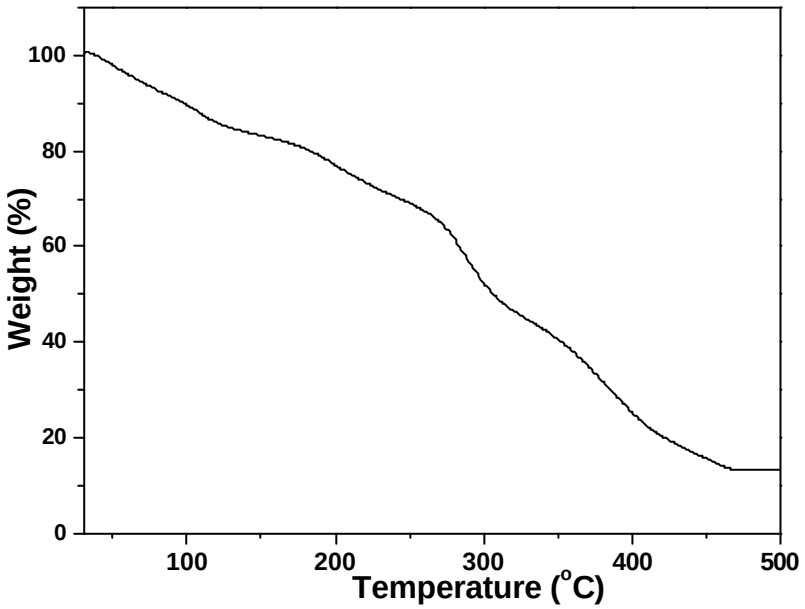


Fig. 10S The TGA plot for compound **2**, **$(Bpyph)_2\{Co(H_2O)_2[Fe(C_2O_4)_3]_2\}\cdot 12.5H_2O$**

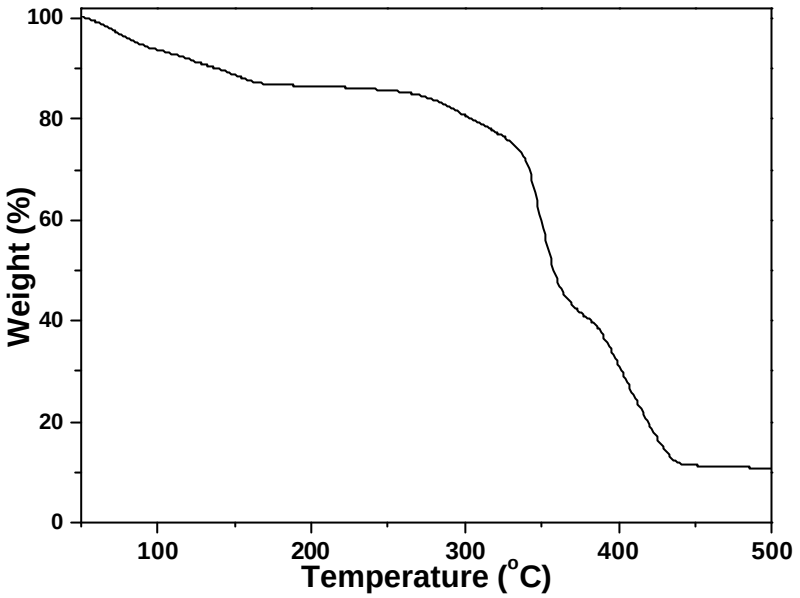


Fig.11S The TGA plot for compound **3**, **(Bpyph)$_2${Mn(H$_2$O)$_2$[Cr(C$_2$O$_4$)$_3$]$_2$}·12.5H$_2$O**

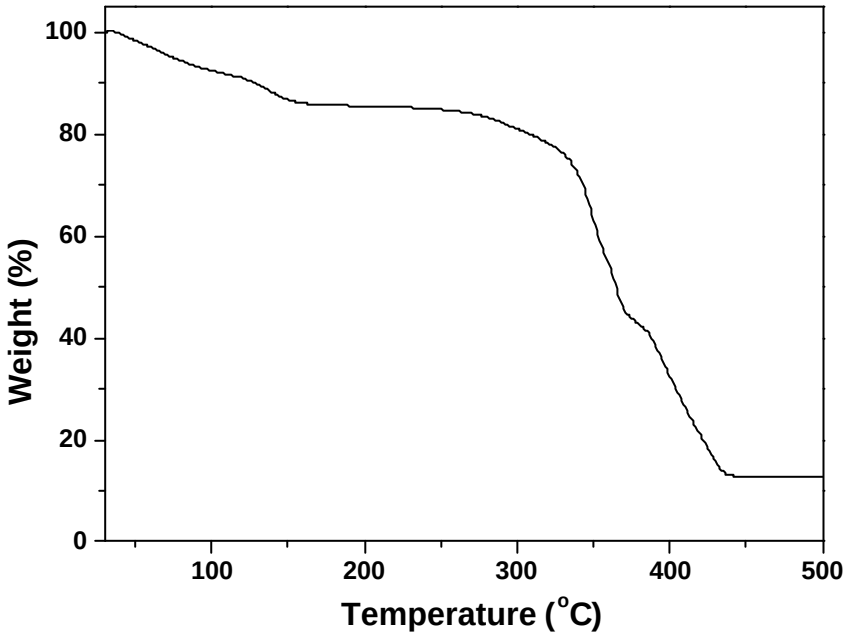


Fig. 12S The TGA plot for compound 4, **(Bpyph)$_2${Co(H$_2$O)$_2$[Cr(C$_2$O$_4$)$_3$]$_2$}·12.5H$_2$O**

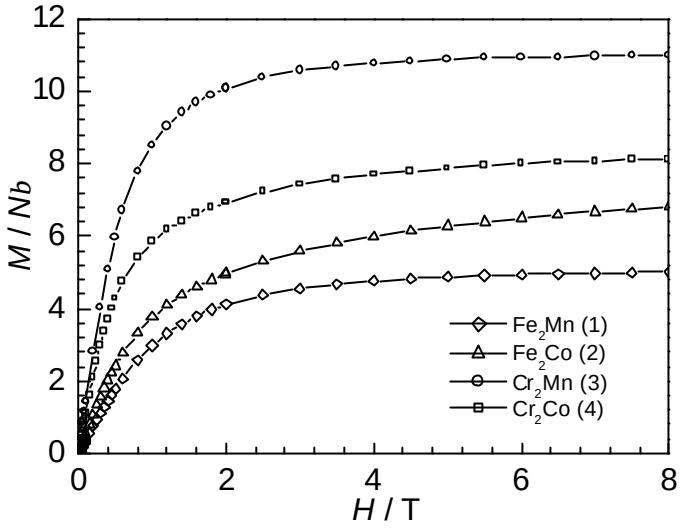


Fig. 13S The field dependence of the magnetization at 2 K for the Fe_2M and Cr_2M series. The solid line is a guide for the eye.

Table 1 Selected bond angles of compounds 1-4

Compound **1**					
O(3)-Fe(1)-O(4)	80.18(8)	O(15)-Fe(2)-O(16)	80.38(8)	O(1)-Mn(1)-O(2)	77.16(7)
O(3)-Fe(1)-O(5)	87.98(9)	O(15)-Fe(2)-O(17)	91.23(9)	O(1)-Mn(1)-O(2W)	91.56(8)
O(3)-Fe(1)-O(9)	88.62(8)	O(15)-Fe(2)-O(21)	92.71(9)	O(1)-Mn(1)-O(13)	102.63(8)
O(3)-Fe(1)-O(10)	98.11(9)	O(15)-Fe(2)-O(22)	88.29(9)	O(2)-Mn(1)-O(14)	102.99(8)
O(4)-Fe(1)-O(5)	89.65(9)	O(16)-Fe(2)-O(17)	101.54(9)	O(13)-Mn(1)-O(14)	77.26(8)
O(4)-Fe(1)-O(6)	89.63(9)	O(16)-Fe(2)-O(18)	89.36(9)	O(1W)-Mn(1)-O(1)	89.17(9)
O(4)-Fe(1)-O(10)	92.84(9)	O(16)-Fe(2)-O(22)	87.42(9)	O(1W)-Mn(1)-O(2)	85.47(8)
O(5)-Fe(1)-O(6)	80.63(9)	O(17)-Fe(2)-O(18)	82.41(10)	O(1W)-Mn(1)-O(13)	92.39(8)
O(5)-Fe(1)-O(9)	97.56(9)	O(17)-Fe(2)-O(21)	90.34(9)	O(1W)-Mn(1)-O(14)	91.79(9)
O(6)-Fe(1)-O(9)	102.79(9)	O(18)-Fe(2)-O(21)	99.04(10)	O(2W)-Mn(1)-O(2)	95.50(8)
O(6)-Fe(1)-O(10)	93.63(9)	O(18)-Fe(2)-O(22)	99.85(10)	O(2W)-Mn(1)-O(13)	86.64(8)
O(9)-Fe(1)-O(10)	81.18(9)	O(21)-Fe(2)-O(22)	80.52(9)	O(2W)-Mn(1)-O(14)	87.47(9)
Compound **2**					
O(3)-Fe(1)-O(4)	80.10(10)	O(15)-Fe(2)-O(16)	80.07(10)	O(1)-Co(1)-O(2)	79.83(9)
O(3)-Fe(1)-O(5)	88.22(11)	O(15)-Fe(2)-O(17)	91.38(11)	O(1)-Co(1)-O(2W)	91.18(9)
O(3)-Fe(1)-O(9)	88.75(10)	O(15)-Fe(2)-O(21)	92.61(11)	O(1)-Co(1)-O(13)	100.13(9)
O(3)-Fe(1)-O(10)	98.84(11)	O(15)-Fe(2)-O(22)	88.12 (11)	O(2)-Co(1)-O(14)	100.04(9)
O(4)-Fe(1)-O(5)	89.79(11)	O(16)-Fe(2)-O(17)	101.55(11)	O(13)-Co(1)-O(14)	80.02(9)
O(4)-Fe(1)-O(6)	90.09(10)	O(16)-Fe(2)-O(18)	89.88(11)	O(1W)-Co(1)-O(1)	89.04(11)
O(4)-Fe(1)-O(10)	92.82(11)	O(16)-Fe(2)-O(22)	87.95(11)	O(1W)-Co(1)-O(2)	86.77(10)
O(5)-Fe(1)-O(6)	80.63(11)	O(17)-Fe(2)-O(18)	82.59(12)	O(1W)-Co(1)-O(13)	91.66(10)
O(5)-Fe(1)-O(9)	97.66(11)	O(17)-Fe(2)-O(21)	89.95(11)	O(1W)-Co(1)-O(14)	91.88(10)
O(6)-Fe(1)-O(9)	102.19(11)	O(18)-Fe(2)-O(21)	98.81(12)	O(2W)-Co(1)-O(2)	93.90(10)
O(6)-Fe(1)-O(10)	92.64(12)	O(18)-Fe(2)-O(22)	99.75(12)	O(2W)-Co(1)-O(13)	87.67(10)
O(9)-Fe(1)-O(10)	81.15(11)	O(21)-Fe(2)-O(22)	80.35(12)	O(2W)-Co(1)-O(14)	87.90(10)
Compound **3**					
O(3)-Cr(1)-O(4)	83.1(3)	O(15)-Cr(2)-O(16)	82.4(4)	O(1)-Mn(1)-O(2)	75.7(3)
O(3)-Cr(1)-O(5)	91.5(4)	O(15)-Cr(2)-O(17)	93.7(4)	O(1)-Mn(1)-O(2W)	90.2(3)
O(3)-Cr(1)-O(9)	91.2(4)	O(15)-Cr(2)-O(21)	94.6(4)	O(1)-Mn(1)-O(13)	102.1(3)
O(3)-Cr(1)-O(10)	93.1(4)	O(15)-Cr(2)-O(22)	89.7(4)	O(2)-Mn(1)-O(14)	104.5(3)

O(4)-Cr(1)-O(5)	87.6(4)	O(16)-Cr(2)-O(17)	95.1(4)	O(13)-Mn(1)-O(14)	77.7(3)
O(4)-Cr(1)-O(6)	89.0(3)	O(16)-Cr(2)-O(18)	87.9(4)	O(1W)-Mn(1)-O(1)	88.7(4)
O(4)-Cr(1)-O(10)	93.8(4)	O(16)-Cr(2)-O(22)	87.9(4)	O(1W)-Mn(1)-O(2)	86.5(4)
O(5)-Cr(1)-O(6)	81.0(4)	O(17)-Cr(2)-O(18)	82.2(4)	O(1W)-Mn(1)-O(13)	90.8(4)
O(5)-Cr(1)-O(9)	96.0(4)	O(17)-Cr(2)-O(21)	90.9(4)	O(1W)-Mn(1)-O(14)	92.2(3)
O(6)-Cr(1)-O(9)	97.1(4)	O(18)-Cr(2)-O(21)	95.5(5)	O(2W)-Mn(1)-O(2)	97.5(3)
O(6)-Cr(1)-O(10)	94.7(3)	O(18)-Cr(2)-O(22)	94.9(4)	O(2W)-Mn(1)-O(13)	85.1(4)
O(9)-Cr(1)-O(10)	82.3(4)	O(21)-Cr(2)-O(22)	86.3(5)	O(2W)-Mn(1)-O(14)	88.9(3)
Compound **4**					
O(3)-Cr(1)-O(4)	82.57(15)	O(15)-Cr(2)-O(16)	82.61(15)	O(1)-Co(1)-O(2)	79.57(14)
O(3)-Cr(1)-O(5)	99.70(18)	O(15)-Cr(2)-O(17)	93.38(18)	O(1)-Co(1)-O(2W)	91.21(15)
O(3)-Cr(1)-O(9)	90.80(16)	O(15)-Cr(2)-O(21)	92.33(18)	O(1)-Co(1)-O(13)	99.98(14)
O(3)-Cr(1)-O(10)	94.81(18)	O(15)-Cr(2)-O(22)	87.93(15)	O(2)-Co(1)-O(14)	100.92(14)
O(4)-Cr(1)-O(5)	87.58(18)	O(16)-Cr(2)-O(17)	95.77(18)	O(13)-Co(1)-O(14)	79.53(14)
O(4)-Cr(1)-O(6)	90.56(16)	O(16)-Cr(2)-O(18)	91.56(17)	O(1W)-Co(1)-O(1)	89.17(18)
O(4)-Cr(1)-O(10)	93.47(10)	O(16)-Cr(2)-O(22)	90.11(18)	O(1W)-Co(1)-O(2)	86.87(16)
O(5)-Cr(1)-O(6)	82.93(19)	O(17)-Cr(2)-O(18)	82.7(2)	O(1W)-Co(1)-O(13)	92.22(16)
O(5)-Cr(1)-O(9)	96.41(18)	O(17)-Cr(2)-O(21)	91.73(19)	O(1W)-Co(1)-O(14)	91.07(16)
O(6)-Cr(1)-O(9)	96.50(18)	O(18)-Cr(2)-O(21)	94.0(2)	O(2W)-Co(1)-O(2)	93.27(16)
O(6)-Cr(1)-O(10)	92.64(19)	O(18)-Cr(2)-O(22)	96.66(19)	O(2W)-Co(1)-O(13)	87.64(16)
O(9)-Cr(1)-O(10)	83.06(17)	O(21)-Cr(2)-O(22)	82.45(19)	O(2W)-Co(1)-O(14)	88.55(17)

Table 2S. hydrogen-bondings for Compound 1, $(Bpyph)_2\{Mn(H_2O)_2[Fe(C_2O_4)_3]_2\}\cdot 12.5H_2O$

D	H	A	Symmetry code	D(D-H)	d(H..A)	d(D..A)	<DHA
O1W	H2	N12	3-x, 0.5+y, 1-z	0.96	1.83	2.780(3)	169.6
O1W	H1	O12W	.	0.71	2.04	2.748(4)	169.2
O2W	H4	N1	-x, 0.5+y, 2-z	0.92	1.89	2.806(3)	175.2
O2W	H3	O5W	.	0.88	1.89	2.754(4)	167.6
O4W	H8	O18	.	0.93	2.05	2.971(4)	170.8
O4W	H7	O7	2-x, 0.5+y, 2-z	0.89	2.10	2.910(4)	152.3
O6W	H12	O9	1-x, 0.5+y, 1-z	0.85	2.05	2.884(3)	168.3
O6W	H11	O23	.	0.88	1.92	2.789(4)	167.6
O12W	H24	O5	.	0.87	2.01	2.846(3)	159.5