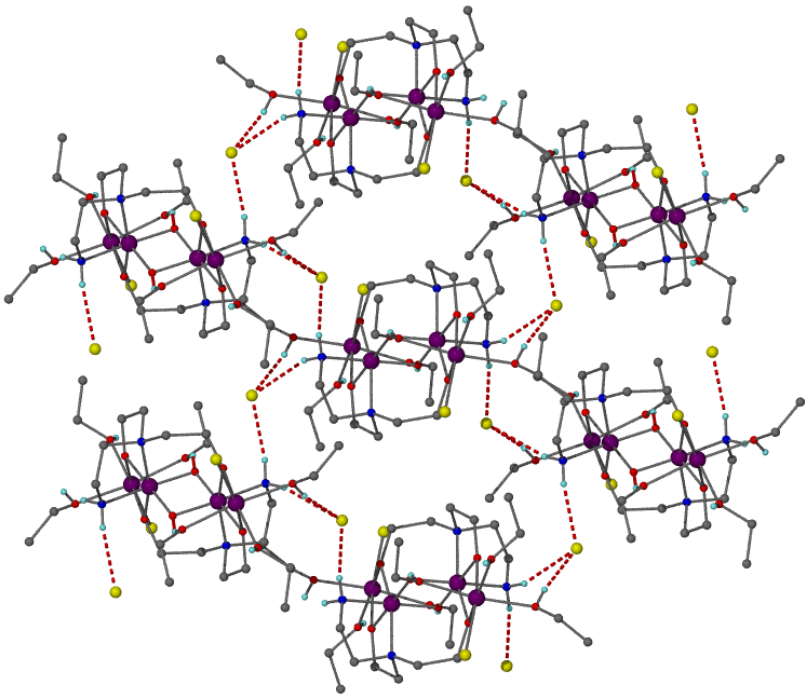

Fig. S1. The H-bonded layer in **1** running parallel to the *bc* plane. Most hydrogen atoms have been omitted for clarity.

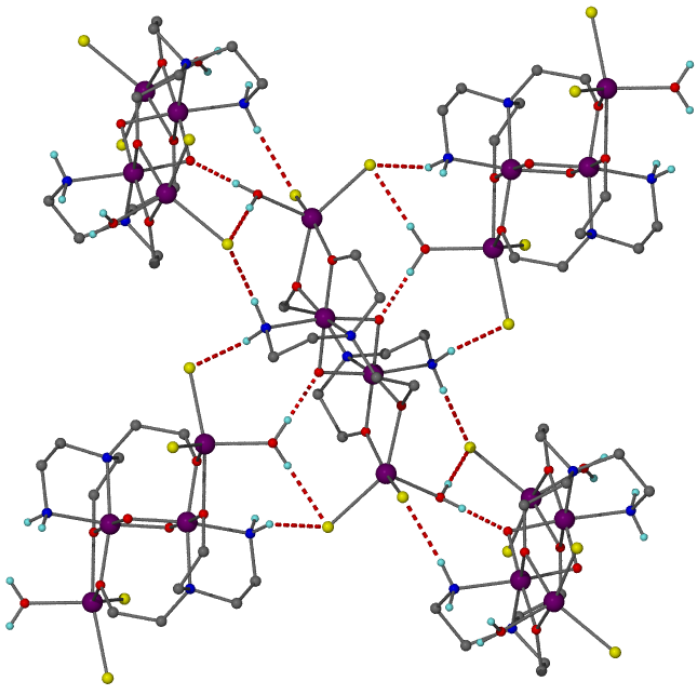

Fig. S2. The H-bonding around **2**. Most hydrogen atoms have been omitted for clarity.

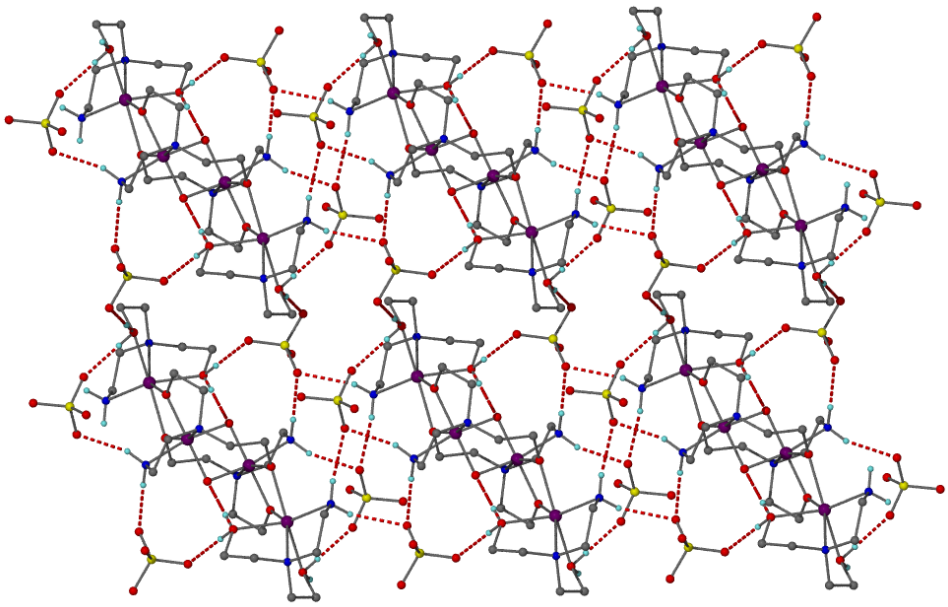

Fig. S3. The H-bonded layer in **3** parallel to the *ab* plane. Most hydrogen atoms have been omitted for clarity.

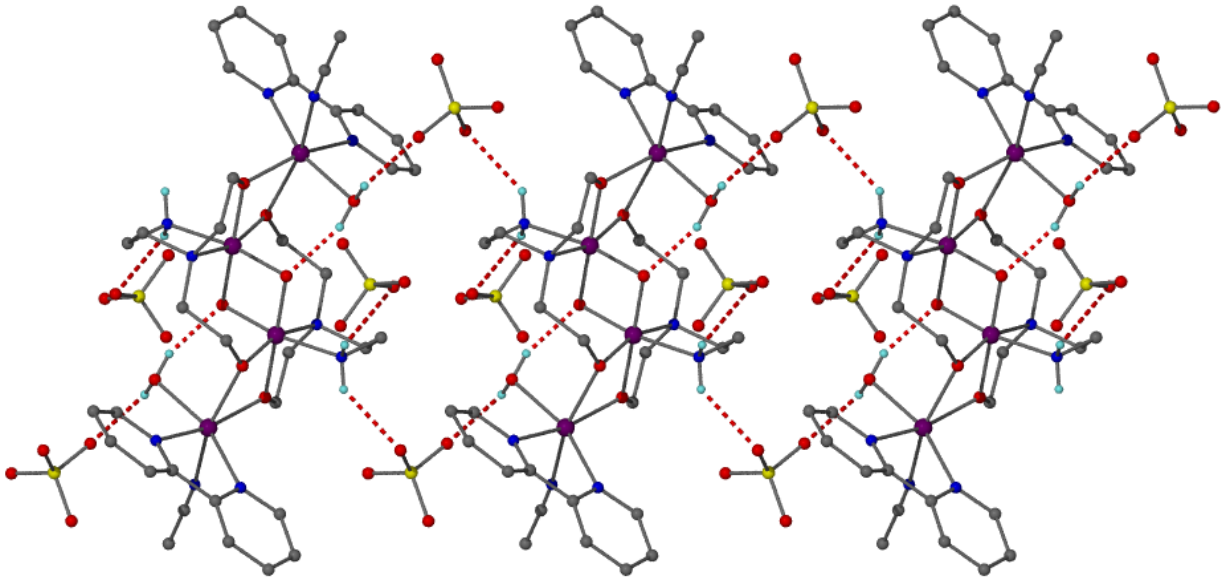

Fig. S4. The H-bonded chain in **4** along the *a* axis. Most hydrogen atoms have been omitted for clarity.

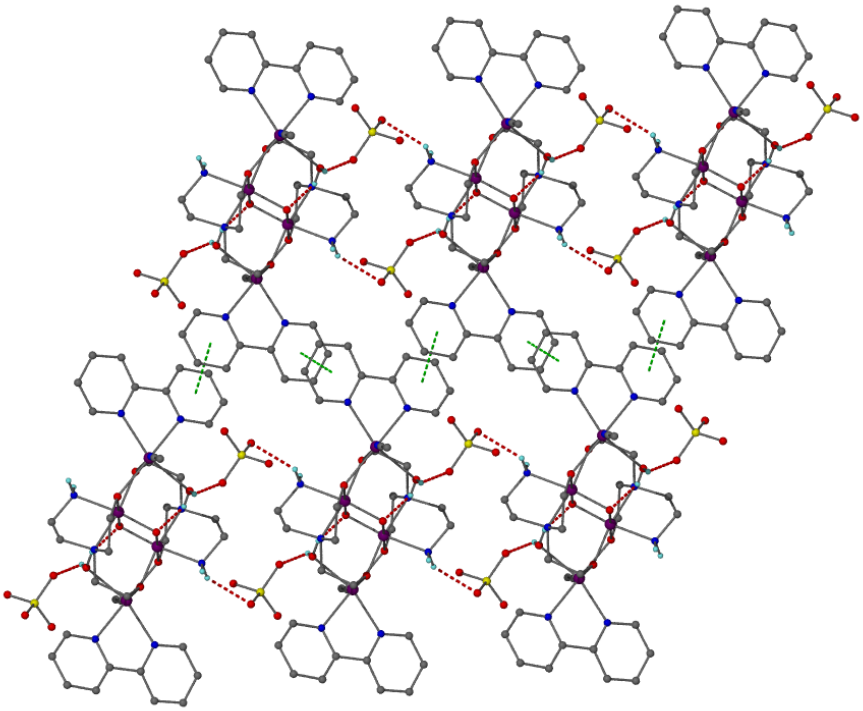

Fig. S5. The 2D layer in **4** parallel to the *ab* plane. Most hydrogen atoms and the singly H-bonded perchlorates have been omitted for clarity.

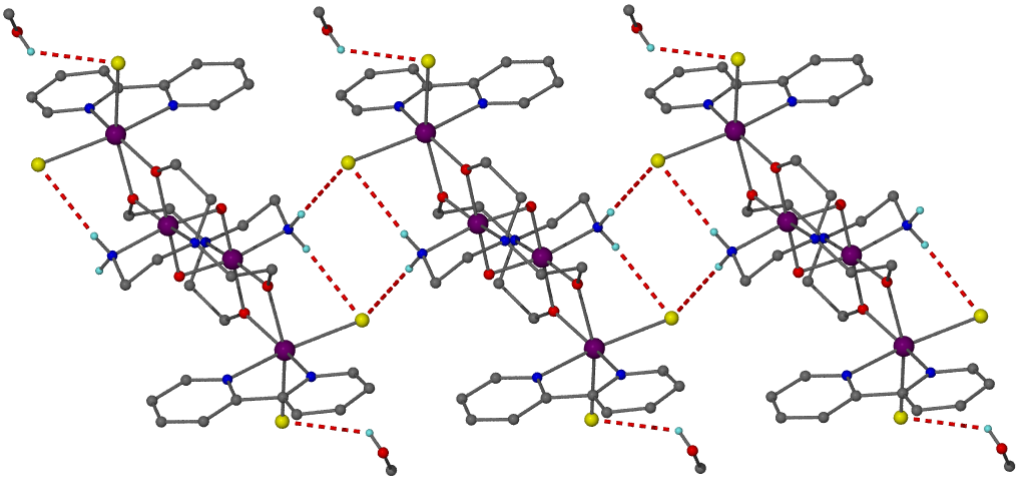

Fig. S6. The H-bonded chain in **5** along the *b* axis. Most hydrogen atoms have been omitted for clarity.

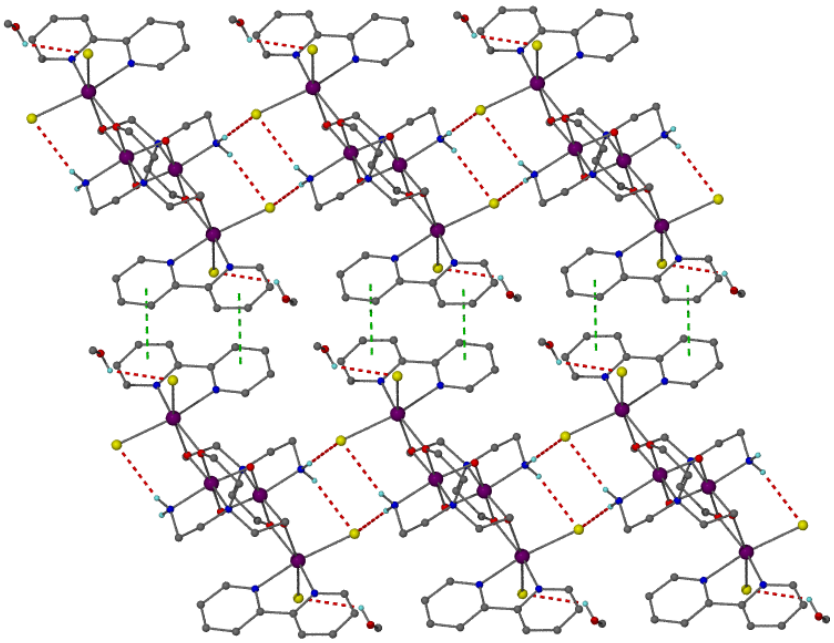

Fig. S7. The 2D layer in **5** parallel to the *bc* plane. Most hydrogen atoms have been omitted for clarity.

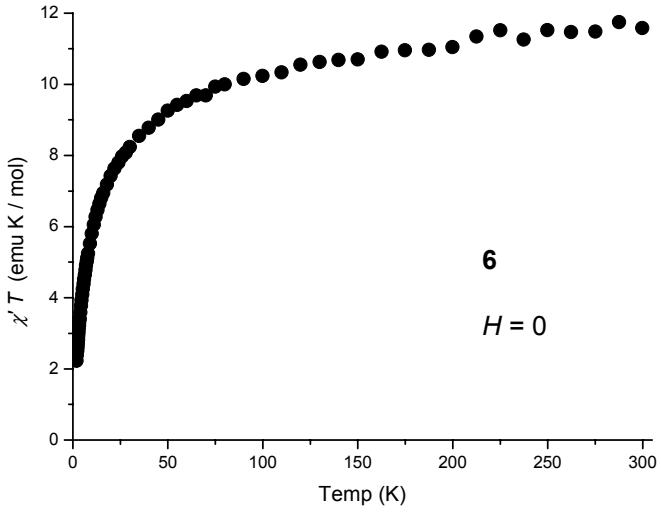

Fig. S8. For **6**, plot of the zero-field $\chi'_m T$ vs. T obtained for an AC frequency $f = 90$ Hz in the 2 K < T < 300 K range. As for the other studied complexes, no evidence of phase transitions is found within this T range.

Table S1: Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for $[Mn^{II}_2Mn^{IV}_2O_2(heed)_2(EtOH)_6Br_2]Br_2$ (**1**)

D^a-H···A^b	D^a···A^b	H···A^b	<D^aHA^b
O12-H9···O1	2.732(3)	1.983(1)	150.7(1)
N231-H23···Br2	3.483(1)	2.626(1)	164.6(1)
N231-H4···Br2 [1-x, 1/2+y, 3/2-z]	3.491(1)	2.660(1)	157.0(1)
O13-H24···Br1 [2-x, 2-y, 1-z]	3.234(1)	2.427(1)	167.9(1)
O14-H28···Br2 [x, 3/2-y, -1/2+z]	3.275(1)	2.454(1)	168.6(1)

[a] D = donor atom.

[b] A = acceptor atom.

Table S2: Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for $[Mn^{II}_2Mn^{IV}_2O_2(heed)_2(H_2O)_2Cl_4]$ (**2**)

D^a-H···A^b	D^a···A^b	H···A^b	<D^aHA^b
N21-H21···Cl13 [1/3+y, 2/3-x+y, 2/3-z]	3.308(1)	2.402(1)	172.7(1)
N21-H22···Cl14 [1/3-x+y, 2/3-x, -1/3+z]	3.315(1)	2.447(1)	159.7(1)
O15-H15···O12 [1/3+x-y, -1/3+x, 2/3-z]	2.601(1)	1.761(1)	179.9(1)
O15-H16···Cl14 [1/3-x+y, 2/3-x, -1/3+z]	3.140(1)	2.299(1)	179.9(1)

[a] D = donor atom. [b] A = acceptor atom.

Table S3: Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for $[Mn^{II}_2Mn^{IV}_2O_2(heed)_2(heedH_2)_2](ClO_4)_4$ (**3**)

D^a-H···A^b	D^a···A^b	H···A^b	<D^aHA^b
N431-H4312···O33 [x,1+y,z]	3.168(1)	2.400(1)	145.3(1)
N431-H4311···O54 [1-x,2-y,1-z]	3.075(1)	2.302(1)	145.4(1)
N432-H4321···O54	3.178(1)	2.298(1)	170.2(1)
N432-H4322···O33 [1-x,1-y,1-z]	3.066(1)	2.242(1)	154.3(1)
N432-H4322···O43 [1-x,1-y,1-z]	3.220(1)	2.448(1)	145.6(1)
O421-H4211[c]···O1 [1-x,1-y,1-z]	2.798(1)	1.957(1)	179.8(1)
O421-H4212[c]···O24 [1-x,1-y,1-z]	3.035(1)	2.196(1)	179.5(1)
O411-H4111[c]···O44 [1+x,y,z]	2.812(1)	1.973(1)	180.0(1)
O411-H4112[c]···O23 [1-x,1-y,1-z]	2.846(1)	2.006(1)	179.7(1)

[a] D = donor atom.

[b] A = acceptor atom.

[c] The hydrogen atoms on O421 (H4211, H4212) and on O411 (H4111, H4112) appear in two positions with 50 % occupancy to satisfy H-bond formation requirements, respectively.

Table S4: Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for $[Mn^{II}_2Mn^{IV}_2O_2(heed)_2(bpy)_2(MeCN)_2(H_2O)_2](ClO_4)_4$ (**4**)

D^a-H···A^b	D^a···A^b	H···A^b	<D^aHA^b
O28-H281···O29 [1-x,-y,2-z]	2.759(1)	1.982(1)	157.3(1)
N12-H121···O34	3.095(1)	2.373(1)	137.8(1)
N12-H122···O38 [1+x,y,z]	3.027(1)	2.291(1)	140.3(1)
O28-H282···O39	2.966(1)	2.217(1)	150.9(1)

[a] D = donor atom.

[b] A = acceptor atom.

Table S5: Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for $[Mn^{II}_2Mn^{IV}_2O_2(heed)_2(bpy)_2Br_4]\cdot 2MeOH$ (**5**·2MeOH)

D^a-H···A^b	D^a···A^b	H···A^b	<D^aHA^b
N26-H261···Br3	3.567(1)	2.803(1)	148.6(1)
N26-H262···Br3 [-x,2-y,1-z]	3.521(1)	2.669(1)	172.1(1)
O29-H291···Br4	3.276(1)	2.682(1)	127.4(1)

[a] D = donor atom.

[b] A = acceptor atom.

Table S6: Dimensions of the unique hydrogen bonds (distances in Å and angles in °) for $\{[Mn^{II}_2Mn^{IV}_2O_2(heed)_2(H_2O)_2(MeOH)_2(dca)_2]Br_2\}_n$ (**6**)

D^a-H···A^b	D^a···A^b	H···A^b	<D^aHA^b
N12-H121···Br24	3.621(1)	2.715(1)	173.4(1)
N12-H122···Br24 [-x,1/2+y,1/2-z]	3.570(1)	2.754(1)	155.5(1)
O14-H142···Br24 [-x,1/2+y,1/2-z]	3.250(1)	2.491(1)	154.2(1)
O16-H162···O13 [-x,2-y,1-z]	2.736(1)	2.017(1)	145.9(1)

[a] D = donor atom.

[b] A = acceptor atom.

Table S7. Bond Valence Sum calculations for complexes **1**-**6**.

Complex **1**					Complex **2**				
Atom	**$Mn^{(II)}$**	**$Mn^{(III)}$**	**$Mn^{(IV)}$**	**Ox.**	**Atom**	**$Mn^{(II)}$**	**$Mn^{(III)}$**	**$Mn^{(IV)}$**	**Ox.**
Mn1	**4.45**	**4.15**	**4.06**	**(IV)**	**Mn1**	**4.43**	**4.13**	**4.04**	**(IV)**
Mn2	**1.99**	**1.86**	**1.83**	**(II)**	**Mn2**	**2.12**	**2.03**	**2.01**	**(II)**
Complex **3**					Complex **4**				
Atom	**$Mn^{(II)}$**	**$Mn^{(III)}$**	**$Mn^{(IV)}$**	**Ox.**	**Atom**	**$Mn^{(II)}$**	**$Mn^{(III)}$**	**$Mn^{(IV)}$**	**Ox.**
Mn1	**1.97**	**1.84**	**1.80**	**(II)**	**Mn1**	**3.68**	**4.13**	**4.05**	**(IV)**
Mn2	**4.46**	**4.16**	**4.07**	**(IV)**	**Mn2**	**2.11**	**2.03**	**1.99**	**(II)**
Complex **5**					Complex **6**				
Atom	**$Mn^{(II)}$**	**$Mn^{(III)}$**	**$Mn^{(IV)}$**	**Ox.**	**Atom**	**$Mn^{(II)}$**	**$Mn^{(III)}$**	**$Mn^{(IV)}$**	**Ox.**
Mn1	**4.45**	**4.15**	**4.06**	**(IV)**	**Mn2**	**4.47**	**4.17**	**4.08**	**(IV)**
Mn2	**1.86**	**1.78**	**1.75**	**(II)**	**Mn4**	**2.21**	**2.08**	**2.03**	**(II)**