Supplementary information for

Room-temperature phosphorescence of manganese-based metal halides

Yue Zhang,[a] Dian Chen,[a] Kai-Hang Jin,[a] Shuang-Quan Zang,[b,*] Qing-Lun Wang[a,*]

[a]*College of Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin, 300071, P. R. China. E-mail address: wangql@nankai.edu.cn (Q.-L. Wang)*

[b]*College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, P. R. China. E-mail address: zangsqzg@zzu.edu.cn (S.-Q.Zang).*

Theoretical calculation:

To evaluate the distortion of the inorganic octahedron, the following equations for the degree of distortion and bond were used:

$$\Delta d = \frac{1}{6}\sum_{n=1}^{6}\frac{(d_n - d)^2}{d}$$

$$\sigma^2 = \frac{1}{11}\sum_{n=1}^{12}(\theta_n - 90°)^2$$

Where θ_n is the X–M–X bond angle, d_n is the M–X bond length, and d is the average value of the M–X bond distances.

References

1. W. Baur, Acta Crystallogr., Sect. B: Struct. *Crystallogr. Cryst. Chem*., 1974, **30**, 1195−1215.
2. K. Robinson, G. V. Gibbs and P. H. Ribbe, *Science*., 1971, **172**, 567.
3. H.-P. Lu, C.-X. Xiao, R.-Y. Song, T.-Y. Li, A. E. Maughan, A. Levin, R. Brunecky, J. J. Berry, D. B. Mitzi, V. Blum and M. C. Beard，*J. Am. Chem. Soc*., 2020, **142**, 13030−13040.
4. Z.-Z. Zhang, J.-C. Jin, L.-K. Gong, Y.-P. Lin, K.-Z. Du and X.-Y. Huang，*Dalton Trans*., 2021, **50**, 3586–3592
5. M.-Y. Li, J.-W. Lin, K.-J. Liu, L.-b. Fan, N. Wang, Z.-N. Guo, W.-X. Yuan, J. Zhao, and Q.-L. Liu，*Inorg. Chem*., 2021, **60**, 11429−11434

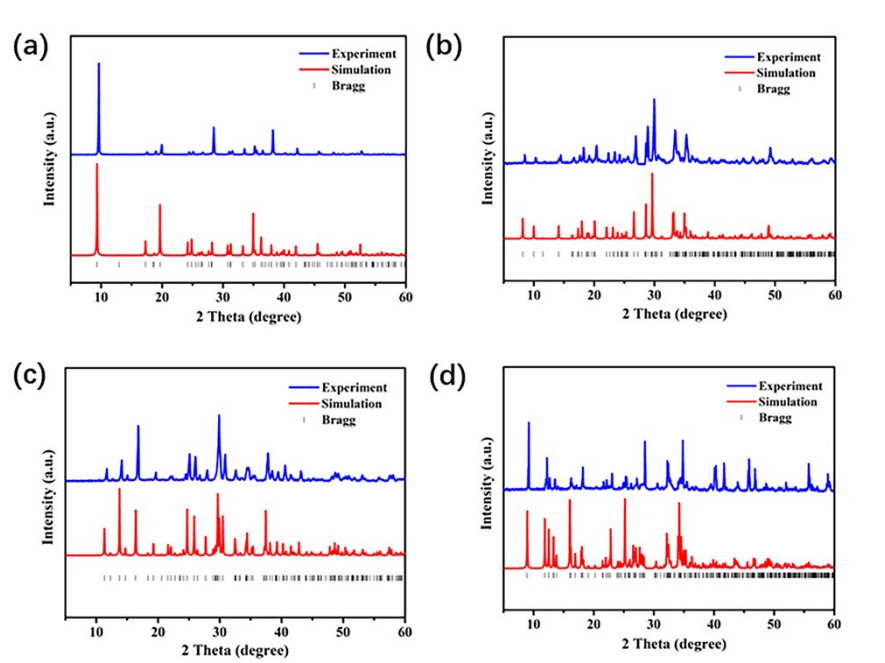

Fig. S1 (a) The simulated and experimental PXRD pattern of $\{[H_2DAP]MnCl_4\}_n$ (**1**); (b) The simulated and experimental PXRD pattern of $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**); (c) The simulated and experimental PXRD pattern of $[H_2TAP]_2MnCl_6$ (**3**); (d) The simulated and experimental PXRD pattern of $[H_2MXD]_2MnCl_6$ (**4**).

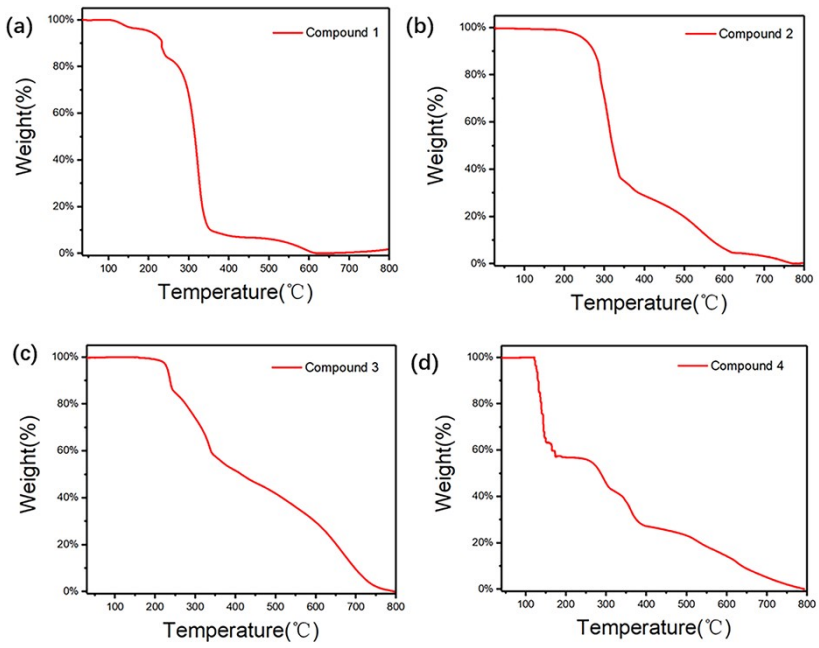

Fig. S2 (a) The thermogravimetric analysis of $\{[H_2DAP]MnCl_4\}_n$ (**1**); (b) The thermogravimetric analysis of $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**); (c) The thermogravimetric analysis of $[H_2TAP]_2MnCl_6$ (**3**); (d) The thermogravimetric analysis of $[H_2MXD]_2MnCl_6$ (**4**).

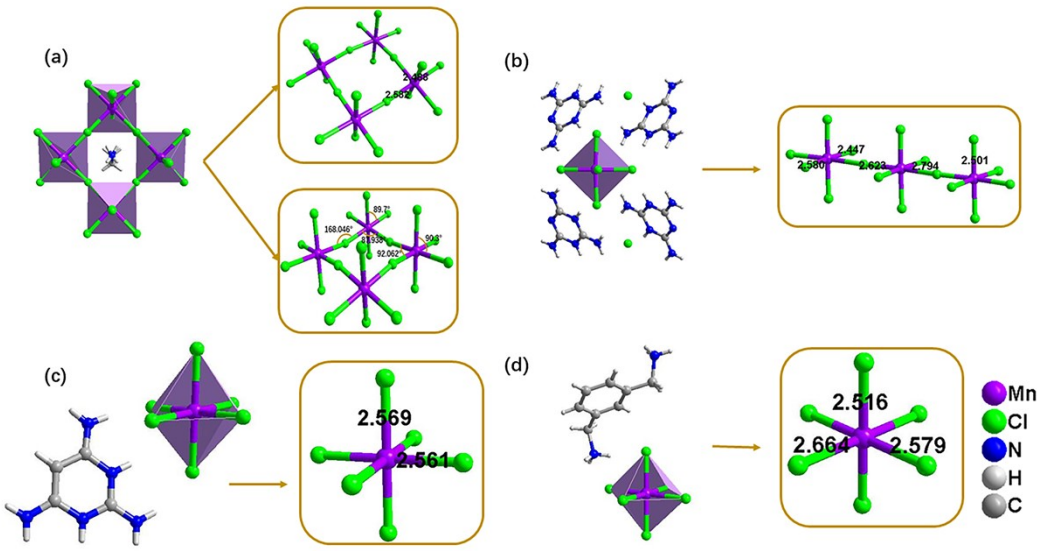

Fig. S3 (a) The smallest asymmetric unit of $\{[H_2DAP]MnCl_4\}_n$ (**1**), as well as the bond length and bond angle; (b) The smallest asymmetric unit of $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**) and the bond length; (c) The smallest asymmetric unit of $[H_2TAP]_2MnCl_6$ (**3**) and the bond length; (d) The smallest asymmetric unit of $[H_2MXD]_2MnCl_6$ (**4**) and the bond length.

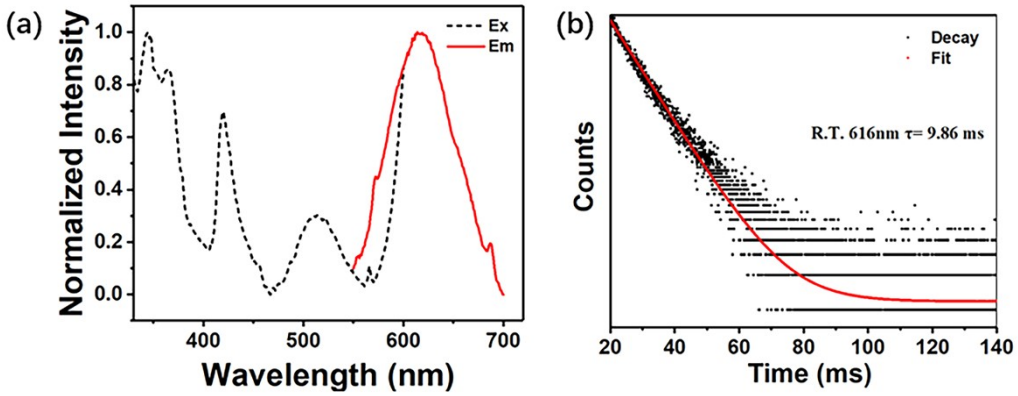

Fig. S4 (a) Excitation and emission spectra of $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**); (b) Decay and fitted curve at room temperature with emission at λ_{em} = 616 nm of $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**). τ is equivalent to the lifetime.

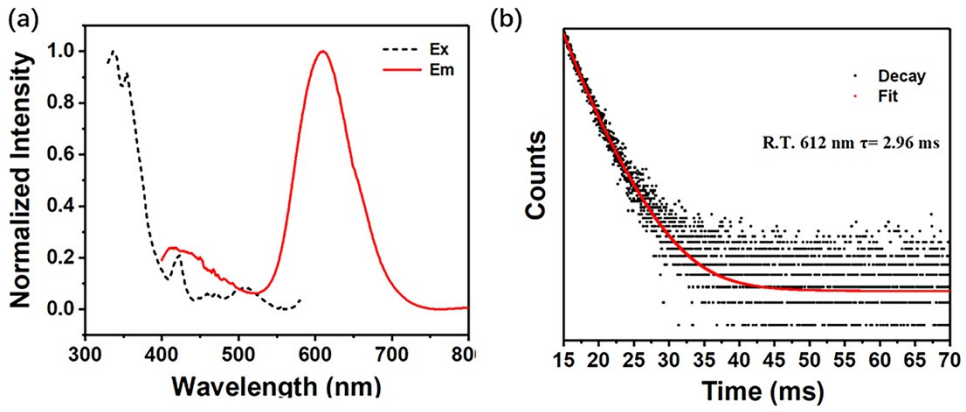

Fig. S5 (a) Excitation and emission spectra of $[H_2TAP]_2MnCl_6$ (**3**); (b) Decay and fitted curve at room temperature with emission at λ_{em} = 612 nm of $[H_2TAP]_2MnCl_6$ (**3**). τ is equivalent to the lifetime.

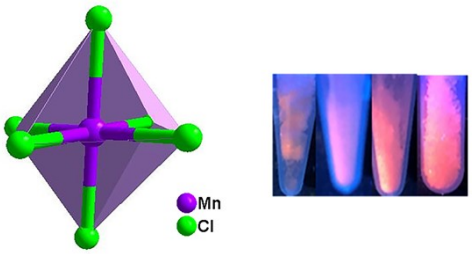

Fig. S6 Comparison of luminescence intensity of $\{[H_2DAP]MnCl_4\}_n$ (**1**), $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**), $[H_2TAP]_2MnCl_6$ (**3**) and $[H_2MXD]_2MnCl_6$ (**4**) at the same excitation wavelength.

Table S1 Crystallographic parameters of $\{[H_2DAP]MnCl_4\}_n$ (**1**) and $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**)

	$\{[H_2DAP]MnCl_4\}_n$ (**1**)	$\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**)
Empirical formula	$C_3H_{12}Cl_4MnN_2$	$C_6H_{16}Cl_6MnN_{12}$
Formula weight	272.89	523.95
Temperature/K	293(2)	293(2)
Crystal system	orthorhombic	monoclinic
Space group	*Imma*	$P2_1/m$
a/Å	7.1701(9)	5.40460(10)
b/Å	18.986(2)	15.3969(4)
c/Å	7.3547(8)	10.8565(3)
α/°	90	90
β/°	90	93.166(2)
γ/°	90	90
Volume/Å^3	1001.2(2)	902.03(4)
Z	4	2
ρ_{calc}g/cm^3	1.810	1.929
μ/mm^{-1}	20.050	14.338
F(000)	548.0	526.0
Crystal size/mm^3	0.03 × 0.03 × 0.02	0.06 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection/°	9.316 to 129.878	8.156 to 147.708
Reflections collected	1344	4101
Independent reflections	481 [R_{int}= 0.0799]	1849 [R_{int}= 0.0424]
Data/restraints/parameters	481/0/33	1849/0/121
Goodness-of-fit on F^2	1.113	1.137
Final *R* indexes [I>=2σ (I)]	R_1= 0.0654, wR_2= 0.1586	R_1 = 0.0576, wR_2 = 0.1676
Final *R* indexes [all data]	R_1= 0.0666, wR_2= 0.1596	R_1 = 0.0611, wR_2 = 0.1694
Largest diff. peak/hole / e Å^{-3}	1.10/-0.55	1.00/-0.85

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S2 Crystallographic parameters of $[H_2TAP]_2MnCl_6$ (**3**) and $[H_2MXD]_2MnCl_6$ (**4**)

	$[H_2TAP]_2MnCl_6$	$[H_2MXD]_2MnCl_6$
Empirical formula	$C_8H_{18}Cl_6MnN_{10}$	$C_{16}H_{28}Cl_6MnN_4$
Formula weight	521.96	544.06
Temperature/K	200.00(10)	296.6(6)
Crystal system	monoclinic	triclinic
Space group	*I2/m*	*P*-1
a/Å	8.9461(3)	7.5206(3)
b/Å	9.6604(3)	8.4873(3)
c/Å	11.2084(3)	10.5291(3)
α/°	90	101.991(3)
β/°	105.229(3)	99.889(3)
γ/°	90	112.943(3)
Volume/Å^3	934.65(5)	581.09(3)
Z	2	1
ρ_{calc}g/cm^3	1.855	1.555
μ/mm^{-1}	13.802	11.160
F(000)	526.0	279.0
Crystal size/mm^3	0.07 × 0.05 × 0.05	0.04 × 0.03 × 0.02
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.5418)
2θ range for data collection/°	11.312 to 146.44	8.98 to 147.562
Reflections collected	1961	4761
Independent reflections	963 [R_{int}= 0.0284]	2227 [R_{int}= 0.0252]
Data/restraints/parameters	963/0/65	2227/0/126
Goodness-of-fit on F^2	1.029	1.100
Final *R* indexes [I>=2σ (I)]	R_1= 0.0375, wR_2= 0.1024	R_1= 0.0376, wR_2= 0.0973
Final *R* indexes [all data]	R_1= 0.0384, wR_2= 0.1031	R_1= 0.0398, wR_2= 0.0981
Largest diff. peak/hole / e Å^{-3}	0.45/-0.53	0.33/-0.68

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S3 The main bond lengths of $\{[H_2DAP]MnCl_4\}_n$ **(1)** (Å)

Bond	Length/Å	Bond	Length/Å
Mn1-Cl1	2.5819(3)	Mn1- $Cl1^3$	2.5819(3)
Mn1- $Cl1^1$	2.5819(3)	Mn1- Cl2	2.4880(15)
Mn1- $Cl1^2$	2.5819(3)	Mn1- $Cl2^1$	2.4880(15)

Table S4 The main bond angles of $\{[H_2DAP]MnCl_4\}_n$ **(1)** (º)

Bonds	Angle /°	Bonds	Angle /°
Cl1-Mn-$Cl1^1$	180.0	$Cl1^1$-Mn-$Cl2^1$	90.31(4)
Cl1-Mn-$Cl1^2$	87.937(12)	$Cl1^2$-Mn-$Cl1^3$	180.00(7)
Cl1-Mn-$Cl1^3$	92.063(12)	$Cl1^2$-Mn-Cl2	90.31(4)
Cl1-Mn-Cl2	90.31(4)	$Cl1^2$-Mn-$Cl2^1$	89.69(4)
Cl1-Mn-$Cl2^1$	89.69(4)	$Cl1^3$-Mn-Cl2	89.69(4)
$Cl1^1$-Mn-$Cl1^2$	92.062(12)	$Cl1^3$-Mn-$Cl2^1$	90.31(4)
$Cl1^1$-Mn-$Cl1^3$	87.938(12)	Cl2-Mn-$Cl2^1$	180.0
$Cl1^1$-Mn-Cl2	90.31(4)		

Table S5 The list of hydrogen bonds in $\{[H_2DAP]MnCl_4\}_n$ **(1)**

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.890	2.456	173.42	3.342	$Cl1^1$
N1-H1B	0.890	2.913	127.99	3.531	Cl1
N1-H1B	0.890	2.872	114.57	3.342	$Cl1^2$
N1-H1B	0.890	2.790	151.25	3.596	$Cl2^3$
N1-H1C	0.890	2.418	144.90	3.188	Cl2

Symmetry codes: [1] [$-x$, $-y+1$, $-z+1$]; [2] [$-x+1/2$, $-y+1$, $z+1/2$]; [3] [$x+1/2$, y, $-z+1/2$].

Table S6 The main bond lengths of $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**) (Å)

Bond	Length/Å	Bond	Length/Å
Mn1-Cl1	2.5015(9)	Mn1- Cl3	2.5797(16)
Mn1- Cl1[1]	2.5015(9)	Mn1- Cl4	2.6226(16)
Mn1- Cl2	2.4467(16)	Mn1- Cl4[2]	2.7939(16)

Table S7 The main bond angles of $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**) (º)

Bonds	Angle /°	Bonds	Angle /°
Cl1-Mn-Cl1[1]	174.25(6)	Cl1[1]-Mn-Cl4[2]	87.82(3)
Cl1-Mn-Cl2	91.83(3)	Cl2-Mn-Cl3	173.68(6)
Cl1-Mn-Cl3	87.94(3)	Cl2-Mn-Cl4	98.81(6)
Cl1-Mn-Cl4	91.91(3)	Cl2-Mn-Cl4[2]	88.77(5)
Cl1-Mn-Cl4[2]	87.82(3)	Cl3-Mn-Cl4	87.51(5)
Cl1[1]-Mn-Cl2	91.83(3)	Cl3-Mn-Cl4[2]	84.90(5)
Cl1[1]-Mn-Cl3	87.94(3)	Cl4-Mn-Cl4[2]	172.42(7)
Cl1[1]-Mn-Cl4	91.91(3)		

Table S8 The list of hydrogen bonds in $\{[(H_2MELA)_2MnCl_5]Cl\}_n$ (**2**)

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.860	2.506	154.38	3.303	Cl4[1]
N1-H1B	0.860	2.744	141.16	3.456	Cl1[2]
N1-H1B	0.860	2.568	136.68	3.248	Cl1[1]
N2-H2	0.860	2.221	163.67	3.055	Cl1[2]
N3-H3	0.860	2.194	173.57	3.050	Cl3[1]
N4-H4A	0.860	2.398	161.32	3.225	Cl5[3]
N4-H4B	0.860	2.362	157.83	3.175	Cl2[2]
N5-H5A	0.860	2.178	175.56	3.036	N6[1]
N5-H5B	0.860	2.527	137.04	3.211	Cl5[4]

Symmetry codes: [1] [-*x*+1, *y*, -*z*+1]; [2] [*x*-1, *y*, *z*]; [3] [-*x*, -*y*+1, -*z*];. [4] [*x*+1, *y*, *z*];

Table S9 The main bond lengths of $[H_2TAP]_2MnCl_6$ (**3**) (Å)

Bond	Length/Å	Bond	Length/Å
Mn1-Cl1	2.5611(8)	Mn1- Cl2[1]	2.5686(6)
Mn1- Cl1[1]	2.5611(8)	Mn1- Cl2[2]	2.5686(6)
Mn1- Cl2	2.5686(6)	Mn1- Cl2[3]	2.5686(6)

Table S10 The main bond angles of $[H_2TAP]_2MnCl_6$ (**3**) (º)

Bonds	Angle /°	Bonds	Angle /°
Cl1-Mn-Cl1[1]	180.0	Cl1[1]-Mn-Cl2[3]	93.481(18)
Cl1-Mn-Cl2	93.482(18)	Cl2-Mn-Cl2[1]	180.0
Cl1-Mn-Cl2[1]	86.518(18)	Cl2-Mn-Cl2[2]	91.12(3)
Cl1-Mn-Cl2[2]	93.482(18)	Cl2-Mn-Cl2[3]	88.88(3)
Cl1-Mn-Cl2[3]	86.518(18)	Cl2[1]-Mn-Cl2[2]	88.88(3)
Cl1[1]-Mn-Cl2	86.518(18)	Cl2[1]-Mn-Cl2[3]	91.12(3)
Cl1[1]-Mn-Cl2[1]	93.481(18)	Cl2[2]-Mn-Cl2[3]	180.0
Cl1[1]-Mn-Cl2[2]	86.519(17)		

Table S11 The list of hydrogen bonds in $[H_2TAP]_2MnCl_6$ (**3**)

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1	0.860	2.984	140.96	3.692	Cl1
N1-H1	0.860	2.707	141.42	3.422	Cl2[1]
N2-H2A	0.860	2.320	172.44	3.174	Cl1
N2-H2B	0.860	2.449	161.30	3.276	Cl2[2]
N3-H3A	0.860	2.391	153.69	3.185	Cl2[1]
N3-H3B	0.860	2.394	153.07	3.185	Cl2[1]
C3-H3	0.930	2.880	138.11	3.626	$Cl2_3$
C3-H3	0.930	2.880	138.11	3.626	$Cl2_4$

Symmetry codes: [1] [-*x*+1, *y*, -*z*+1]; [2] [-*x*+3/2, -*y*+1/2, -*z*+1/2]; [3] [-*x*+3/2, -*y*+1/2, -*z*+1/2];. [4] [-*x*+3/2, *y*-1/2, -*z*+1/2];

Table S12 The main bond lengths of $[H_2MXD]_2MnCl_6$ (**4**) (Å)

Bond	Length/Å	Bond	Length/Å
Mn1-Cl1	2.5787(4)	Mn1- Cl2[1]	2.5138(5)
Mn1- Cl1[1]	2.5786(4)	Mn1- Cl3	2.6628(5)
Mn1- Cl2	2.5138(5)	Mn1- Cl3[1]	2.6627(5)

Table S13 The main bond angles of $[H_2MXD]_2MnCl_6$ (**4**) (º)

Bonds	Angle /°	Bonds	Angle /°
Cl1-Mn-Cl1[1]	180.0	Cl1[1]-Mn-Cl3[1]	90.149(15)
Cl1-Mn-Cl2	88.831(16)	Cl2-Mn-Cl2[1]	180.0
Cl1-Mn-Cl2[1]	91.169(16)	Cl2-Mn-Cl3	88.414(17)
Cl1-Mn-Cl3	90.149(15)	Cl2-Mn-Cl3[1]	91.587(17)
Cl1-Mn-Cl3[1]	89.852(15)	Cl2[1]-Mn-Cl3	91.586(17)
Cl1[1]-Mn-Cl2	91.168(16)	Cl2[1]-Mn-Cl3[1]	88.413(17)
Cl1[1]-Mn-Cl2[1]	88.832(16)	Cl3-Mn-Cl3[1]	180.0
Cl1[1]-Mn-Cl3	89.851(15)		

Table S14 The list of hydrogen bonds in $[H_2MXD]_2MnCl_6$ (**4**)

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1A	0.890	2.557	126.78	3.171	Cl1
N1-H1A	0.890	2.728	136.04	3.425	Cl3[1]
N1-H1B	0.890	2.835	113.86	3.297	Cl1[2]
N1-H1B	0.890	2.418	149.6	3.218	Cl2[1]
N1-H1C	0.890	2.391	164.41	3.257	Cl3[3]
N2-H2A	0.890	2.72	122.01	3.28	Cl1[4]
N2-H2A	0.890	2.439	150.73	3.245	Cl2[4]
N2-H2B	0.890	2.413	155.96	3.246	Cl1[5]
N2-H2C	0.890	2.585	136	3.284	Cl3[6]
N2-H2C	0.890	2.917	114.56	3.385	Cl3[4]

Symmetry codes: [1] [*x*+1, *y*, *z*]; [2] [-*x*+1, -*y*+1, -*z*]; [3] [-*x*, -*y*+1, -*z*];. [4] [-*x*+1, -*y*+1, -*z*+1]; [5] [*x*+1, *y*+1, *z*+1]; [6] [*x*+2, *y*+1, *z*+1]