Single-molecular magnet achieved through topological tuning by sodium ion

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Table S1. Crystallographic data and structural refinement parameters for complexes **1-3**.

Complex	**1**	**2**	**3**
Empirical Sormula	$C_{38}H_{39}Mn_3N_8O_{24}$	$C_{45}H_{51}Mn_3N_6Na_2O_{21}$	$C_{70}H_{81}Mn_6N_{12}Na_3O_{47}$
Formula weight / g·mol^{-1}	1156.59	1222.71	2241.07
Temperature / K	153(2)	153(2) K	153(2) K
Wavelength / Å	0.71073	0.71073 A	0.71073 A
Crystal system	Triclinic	Triclinic	Trigonal
Space group	$P\bar{1}$	$P\bar{1}$	R-3
a / Å	11.6155(4)	13.5021(7)	16.918(10)
b / Å	13.4396(6)	14.1079(8)	16.918(10)
c / Å	16.6802(8)	15.3728(7)	28.201(3)
α / º	86.026(4)	84.810(4)	90
β / º	75.057(3)	68.896(4)	90
γ / º	85.102(5)	77.273(5)	120
V / Å^3	2503.64(19)	2664.6(2)	7026.6(11)
Z	2	2	3
ρ_{calc} / g cm^{-3}	1.534	1.524	1.589
μ / mm^{-1}	0.835	0.799	0.900
θ range for data / °	3.438 to 28.794	3.286 to 25.009	2.002 to 25.007
F(000)	1180	1256	3432
Crystal size / mm	0.30 × 0.25 × 0.18	0.24 × 0.19 × 0.16	0.28 × 0.23 × 0.18
Reflections collected	26750	23836	23530
Reflections unique	11576	9216	2710
R_{int}	0.0586	0.0572	0.0267
Max. / min. transmission	0.860 and 0.778	0.880 and 0.833	0.850 and 0.780
Data / restraints / parameters	11576 / 71 / 686	9216 / 119 / 731	2710 / 2 / 225
Goodness-of-fit	1.079	1.139	1.057
R_1 ($I > 2\sigma(I)$) [a]	0.0920	0.0687	0.0314
wR_2 ($I > 2\sigma(I)$) [b]	0.2347	0.1675	0.0834
R_1 (all data) [a]	0.1710	0.0895	0.0355
wR_2 (all data) [b]	0.2937	0.1847	0.0881
Largest diff. Peak, hole / (e Å^{-3})	0.989 and -0.464	1.863 and -1.329	0.493 and -0.671

[a] $R_1 = \Sigma \, ||Fo| - |Fc|| / \Sigma |Fo|$; [b] $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2 / \Sigma w(Fo^2)^2]^{½}$.

Table S2. Bond lengths [Å] and angles [º] for **1**.

Mn1-O1	1.857(4)	Mn2-N4	2.018(5)
Mn1-O3	1.901(4)	Mn2-O13	2.208(4)
Mn1-O10	1.936(4)	Mn2-O15	2.283(5)
Mn1-N2	2.019(5)	Mn2-Mn3	3.1862(13)
Mn1-O12	2.248(4)	Mn3-O1	1.884(4)
Mn1-O11	2.250(4)	Mn3-O9	1.906(4)
Mn1-Mn2	3.2393(13)	Mn3-O7	1.940(5)
Mn2-O6	1.889(4)	Mn3-N6	2.027(5)
Mn2-O1	1.899(4)	Mn3-O14	2.145(4)
Mn2-O4	1.929(4)	Mn3-O16	2.325(6)
O1-Mn1-O3	172.07(19)	O4-Mn2-O13	97.17(18)
O1-Mn1-O10	92.84(17)	N4-Mn2-O13	85.37(18)
O3-Mn1-O10	86.28(18)	O6-Mn2-O15	89.1(2)
O1-Mn1-N2	90.10(18)	O1-Mn2-O15	91.6(2)
O3-Mn1-N2	91.64(18)	O4-Mn2-O15	92.4(2)
O10-Mn1-N2	173.2(2)	N4-Mn2-O15	85.1(2)
O1-Mn1-O12	85.49(17)	O13-Mn2-O15	170.40(17)
O3-Mn1-O12	86.77(18)	O1-Mn3-O9	179.4(2)
O10-Mn1-O12	96.30(17)	O1-Mn3-O7	93.30(17)
N2-Mn1-O12	90.03(18)	O9-Mn3-O7	86.7(2)
O1-Mn1-O11	101.14(16)	O1-Mn3-N6	88.42(18)
O3-Mn1-O11	86.71(17)	O9-Mn3-N6	91.5(2)
O10-Mn1-O11	87.71(17)	O7-Mn3-N6	172.3(2)
N2-Mn1-O11	85.72(18)	O1-Mn3-O14	89.07(16)
O12-Mn1-O11	172.11(15)	O9-Mn3-O14	91.51(19)
O6-Mn2-O1	176.97(17)	O7-Mn3-O14	92.59(18)
O6-Mn2-O4	85.14(18)	N6-Mn3-O14	94.99(19)
O1-Mn2-O4	91.88(17)	O1-Mn3-O16	91.1(2)
O6-Mn2-N4	92.2(2)	O9-Mn3-O16	88.3(3)
O1-Mn2-N4	90.84(19)	O7-Mn3-O16	89.6(2)
O4-Mn2-N4	176.4(2)	N6-Mn3-O16	82.8(2)
O6-Mn2-O13	92.46(19)	O14-Mn3-O16	177.8(2)
O1-Mn2-O13	87.37(17)		
Mn1-O1-Mn3	120.7(2)	Mn3-O7-N4-Mn2	28.5(5)
Mn1-O1-Mn2	119.18(19)	Mn1-O10-N6-Mn3	-1.8(5)
Mn3-O1-Mn2	114.8(2)	Mn2-O4-N2-Mn1	2.7(6)

Table S3 Bond lengths [Å] and angles [º] for **2**.

Mn1-O1	1.876(3)	Mn3-O15	2.191(3)
Mn1-O3	1.907(3)	Na1-O17A	2.322(4)
Mn1-O16	1.998(3)	Na1-O17	2.322(4)
Mn1-N2	2.034(4)	Na1-O16A	2.422(3)

Mn1-O10	2.127(3)	Na1-O16	2.422(3)
Mn1-O11	2.224(3)	Na1-O3A	2.489(3)
Mn1-Mn3	3.1979(9)	Na1-O3	2.489(3)
Mn1-Mn2	3.2322(10)	Na2-O18	2.316(4)
Mn2-O1	1.883(3)	Na2-O18B	2.316(4)
Mn2-O6	1.892(3)	Na2-O6	2.435(3)
Mn2-O12	2.017(3)	Na2-O6B	2.435(3)
Mn2-N4	2.051(4)	Na2-O12B	2.624(3)
Mn2-O4	2.134(3)	Na2-O12	2.624(3)
Mn2-O13	2.237(3)	Na3-O191	2.141(10)
Mn2-Mn3	3.2221(10)	Na3-O15	2.392(4)
Mn3-O1	1.863(3)	Na3-O8C	2.467(5)
Mn3-O9	1.910(3)	Na3-O9	2.549(5)
Mn3-O14	2.014(3)	Na3-O14	2.706(5)
Mn3-N6	2.053(4)	Na3-O192	2.779(12)
Mn3-O7	2.083(4)	Na3-O20	2.838(13)
O1-Mn1-O3	177.63(14)	O12-Mn2-O13	88.78(13)
O1-Mn1-O16	95.00(13)	N4-Mn2-O13	83.90(14)
O3-Mn1-O16	84.34(13)	O4-Mn2-O13	174.84(13)
O1-Mn1-N2	89.67(14)	O1-Mn3-O9	178.92(15)
O3-Mn1-N2	91.14(14)	O1-Mn3-O14	94.39(14)
O16-Mn1-N2	174.16(14)	O9-Mn3-O14	84.92(14
O1-Mn1-O10	88.67(13)	O1-Mn3-N6	89.60(14)
O3-Mn1-O10	89.11(13)	O9-Mn3-N6	90.96(15)
O16-Mn1-O10	94.31(14)	O14-Mn3-N6	170.69(16)
N2-Mn1-O10	89.30(14)	O1-Mn3-O7	89.69(14)
O1-Mn1-O11	88.99(13)	O9-Mn3-O7	91.17(14)
O3-Mn1-O11	93.26(13)	O14-Mn3-O7	92.91(15)
O16-Mn1-O11	89.13(13)	N6-Mn3-O7	95.52(15)
N2-Mn1-O11	87.43(14)	O1-Mn3-O15	90.14(13)
O10-Mn1-O11	176.00(13)	O9-Mn3-O15	88.97(14)
O1-Mn2-O6	177.86(14)	O14-Mn3-O15	83.54(14)
O1-Mn2-O12	96.23(14)	N6-Mn3-O15	88.05(14)
O6-Mn2-O12	83.70(14)	O7-Mn3-O15	176.42(14)
O1-Mn2-N4	89.79(15)	Mn3-Mn1-Mn2	60.14(2)
O6-Mn2-N4	90.58(16)	Mn3-Mn2-Mn1	59.40(2)
O12-Mn2-N4	170.30(15)	Mn1-Mn3-Mn2	60.46(2)
O1-Mn2-O4	87.85(13)	Mn3-O1-Mn1	117.56(16)
O6-Mn2-O4	90.00(14)	Mn3-O1-Mn2	118.65(15)
O12-Mn2-O4	90.27(13)	Mn1-O1-Mn2	118.59(16)
N4-Mn2-O4	97.58(14)	Mn2-O4-N2-Mn1	0.6(4)
O1-Mn2-O13	87.21(13)	Mn3-O7-N4-Mn2	6.7(4)
O6-Mn2-O13	94.93(14)	Mn1-O10-N6-Mn3	8.3(4)

Symmetry codes: A) $-x + 1, -y + 1, -z + 2$; B) $-x + 2, -y, -z + 2$; C) $-x + 2, -y + 1, -z + 1$

Table S4 Bond lengths [Å] and angles [º] for **3**.

Mn1-O1	1.8884(5)	Na1-O7	2.3098(17)
Mn1-O3	1.9219(14)	Na1-O7C	2.3098(17)
Mn1-O5	1.9932(14)	Na1-O3	2.4463(14)
Mn1-N2	2.0179(17)	Na1-O3C	2.4464(14)
Mn1-O4A	2.1261(14)	Na1-O5C	2.4990(14)
Mn1-O6B	2.2205(14)	Na1-O5	2.4991(14)
Mn1-Mn1B	3.2315(5)	Mn1-Mn1A	3.2315(5)
O1-Mn1-O3	177.79(7)	O1-Mn1-O6B	86.83(6)
O1-Mn1-O5	95.25(7)	O3-Mn1-O6B	95.34(6)
O3-Mn1-O5	85.24(6)	O5-Mn1-O6B	87.52(6)
O1-Mn1-N2	89.47(7)	N2-Mn1-O6B	88.35(6)
O3-Mn1-N2	90.22(6)	O4A-Mn1-O6B	175.62(5)
O5-Mn1-N2	173.55(6)	Mn1B-Mn1-Mn1A	60.0
O1-Mn1-O4A	88.88(6)	Mn1B-O1-Mn1A	117.66(4)
O3-Mn1-O4A	88.94(6)	Mn1B-O1-Mn1	117.66(4)
O5-Mn1-O4A	93.75(6)	Mn1A-O1-Mn1	117.66(4)
N2-Mn1-O4A	90.74(6)	Mn1B-O4-N2-Mn1	-6.52(17)

Symmetry codes: A) $-y + 1, x - y, z$; B) $-x + y + 1, -x + 1, z$; C) $-x + 1, -y + 1, -z$.

T**able S5** Hydrogen bonds for **1-3** [Å and º].

complex	D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
1	O11-H111...O13	0.86	2.43	3.106(6)	136.0
	O11-H112...O18	0.84	2.62	3.335(7)	144.5
	O11-H112...N7	0.84	2.20	2.919(7)	143.3
	O12-H121...O3A	0.80	2.06	2.697(6)	136.7
	O12-H122...N1A	0.87	2.58	3.203(8)	129.6
	C29-H29B...O17B	0.98	2.63	3.459(8)	142.8
	O15-H151...O22	0.83	2.41	2.887(10)	116.7
	O16-H161...O22	0.84	2.05	2.738(12)	139.1
	O16-H162...O2WC	0.84	2.29	3.09(2)	160.5
	O17-H171...O13	0.82	1.83	2.591(5)	154.4
	O19-H19A...O1W	0.84	1.86	2.699(18)	176.7
	O20-H201...O21D	0.87	2.15	2.802(10)	131.4
	O20-H202...O18E	0.85	2.50	3.350(10)	178.3
	O21-H211...O26F	0.83	2.22	2.70(2)	116.3
	O21-H212...O5	0.85	1.92	2.718(8)	155.1
	O22-H221...O23	0.85	1.83	2.665(15)	165.1
	O22-H222...O21F	0.85	1.81	2.658(11)	173.7
	O23-H231...N8G	0.84	2.21	2.978(17)	150.4
	O23-H232...O18G	0.86	2.55	3.167(12)	130.0
	O23-H232...O2W	0.86	2.22	2.87(3)	132.0
	O26-H261...O27H	0.85	1.79	2.35(3)	121.5
	O26-H261...O27A	0.85	2.12	2.77(4)	134.6

	O26-H262...O16	0.85	2.50	3.349(18)	175.9
	O27-H271...O2	0.84	2.05	2.80(2)	148.5
	O27-H272...O1W	0.85	1.95	2.80(3)	177.2
	O1W-H1WB...O9I	0.90	2.30	2.863(8)	120.9
	O1W-H1WA...O26I	0.90	2.09	2.55(3)	110.4
	O1W-H1WB...O9I	0.90	2.30	2.863(8)	120.9
	O1W-H1WB...N5I	0.90	2.43	3.076(14)	129.7
	O2W-H2WA...N1G	0.90	2.29	2.903(9)	124.9
	O2W-H2WA...O16C	0.90	2.43	3.09(2)	129.8
	O2W-H2WA...N1G	0.90	2.29	2.903(9)	124.9
	O2W-H2WB...O20J	0.91	2.10	2.70(3)	122.9
	Symmetry codes: A) -*x* + 1, -*y* + 1, -*z*; B) -*x* + 1, -*y* + 1, -*z* + 1; C) -*x* + 1, -*y*, -*z*; D) *x* + 1, *y*, *z* - 1; E) -*x* + 2, -*y* + 1, -*z*; F) -*x* +1, -*y*, -*z* + 1; G) *x*, *y* - 1, *z*; H) *x* + 1, *y* - 1, *z*; I) *x* - 1, *y* + 1, *z*; J) -*x* + 2, -*y*, -*z*.				
2	O17-H17A...O11A	0.85	2.00	2.815(5)	160.8
	O18-H18A...O13B	0.84	2.01	2.841(5)	170.3
	O18-H18B...O2D	0.84	2.31	2.865(5)	124.4
	O191-H191...O5E	0.86	2.44	3.212(13)	148.8
	O191-H191...O8C	0.86	2.50	3.046(12)	121.5
	Symmetry codes: A) -*x* + 1, -*y* + 1, -*z* + 2; B) -*x* + 2, -*y*, -*z* + 2; C) -*x* + 2, -*y* + 1, -*z* + 1; D) -*x* + 1, -*y*, -*z* + 2; E) *x*, *y* + 1, *z*.				
3	O1-H1...O9	0.86	2.57	3.427(10)	180.0
	O7-H71...O2E	0.85	2.05	2.888(2)	173.0
	O8-H81...N1F	0.85	2.59	3.135(4)	123.2
	O8-H82...O8F	0.85	2.34	3.193(4)	173.9
	O11-H11...O11G	0.86	1.61	2.44(4)	159.8
	O11-H11...O11D	0.86	1.10	1.70(3)	119.7
	Symmetry codes:D) *x* – *y* + 1/3, *x* – 1/3, -*z* + 2/3; E) *y* – 1/3, –*x* + *y* + 1/3, -*z* + 1/3; F) *x* – y + 2/3, *x* + 1/3, –*z* + 1/3; G) –*x* + 4 /3, –*y* + 2/3, –*z* + 2/3.				

T**able S6 *π*-*π*** stacking interactions in **1** and **2** (Å)

Complex	ring(1)···ring(2)	d[Cg(1)···Cg(2)][1]	α[2]	β[3]	γ[4]	d[Cg(1)···P(2)][5]	d[Cg(2)···P(1)][6]
1	C1 ~ C5…C22 ~ C27	3.4125(2)	6	9.5	11	-3.349	-3.366
	C1 ~ C5…C30 ~ C34	3.8243(2)	8	26	34	-3.175	3.4496
	C10 ~ C14…C13~ C18	3.4067(2)	3	13	14	-3.301	-3.324
	C19 ~ C23…C22 ~ C27	3.3449(2)	0	4.2	4.3	3.3354	3.336
	C4~ C9…C30 ~ C34	3.5166(2)	7	13	11	-3.451	3.4296
	C13~ C18…C10 ~ C14	3.4067(2)	3	14	13	-3.324	-3.301
	C13~ C18…C13 ~ C15	3.7291(2)	0	26	26	-3.34	-3.34
	C13~ C18…C30 ~ C34	3.5462(2)	7	20	12	3.463	3.3433
	C13~ C18…C33 ~ C38	3.7248(2)	6	16	22	3.4641	3.5862
	C22 ~ C27…C22 ~ C27	3.8808(2)	0	31	31	3.3362	3.3362
2	C1 ~ C4,C9…C4 ~ C9	3.4014(2)	3	7.1	9.4	-3.356	-3.376
	C10 ~C13, C18…C13 ~ C18	3.8007(2)	1	26	27	3.3979	3.4166
	C4 ~ C9…C4 ~ C9	3.7816(2)	0	26	26	-3.393	-3.393
	C13 ~ C18…C13 ~ C18	3.8555(2)	0	28	28	3.4046	3.4046
	C22 ~ C27…C22 ~ C27	3.8090(2)	0	25	25	-3.443	-3.443

[1]Centroid–centroid distance. [2]Dihedral angle between the ring planes. [3]Angle between the centroid vector Cg(1)…Cg(2) and the normal to the plane 2. [4]Angle between the centroid vector Cg(1)…Cg(2) and the normal to the plane 1. [5] Perpendicular distance of Cg(1) on ring plane 2. [6]Perpendicular distance of Cg(2) on ring plane 1.

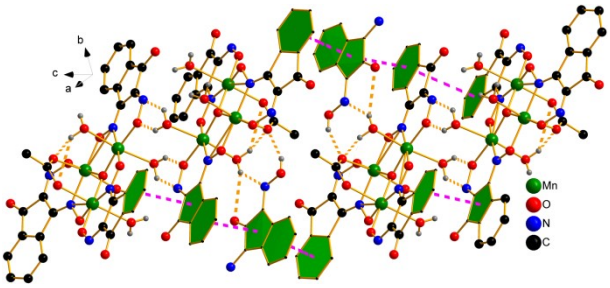

Fig. S1 A show of the hydrogen bonds and π···π stacking interactions in the supramolecular one-dimensional chain of **1**.

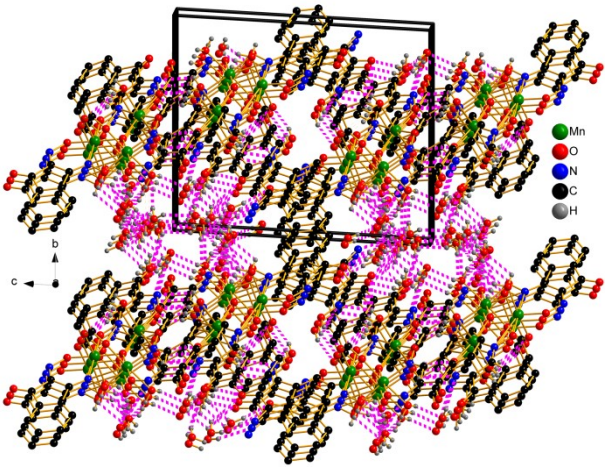

Fig. S2 A show of the hydrogen bonds and π···π stacking interactions in the supramolecular three-dimensional of **1**.

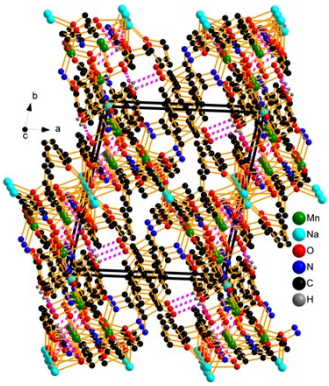

Fig. S3 A show of the hydrogen bonds and π···π stacking interactions in the supramolecular three-dimensional of **2**.

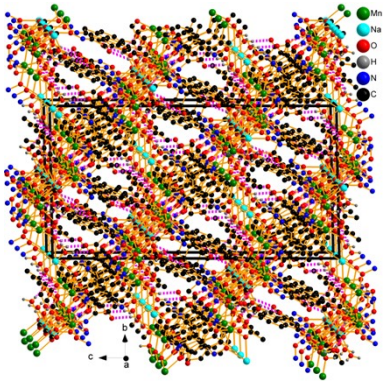

Fig. S4 A show of the hydrogen bonds stacking interactions in the supramolecular three-dimensional of **3**.

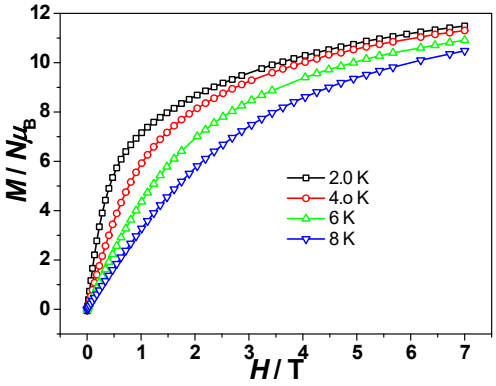

Fig. S5 Experimental *M* vs. *H* plots at the indicated temperatures for **3**.

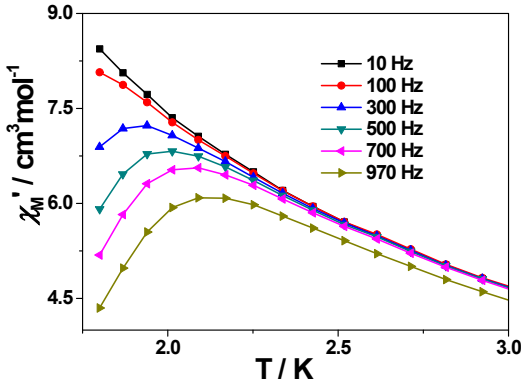

Fig. S6 Temperature-dependent χ_M' AC susceptibilities under zero DC field for **3**.

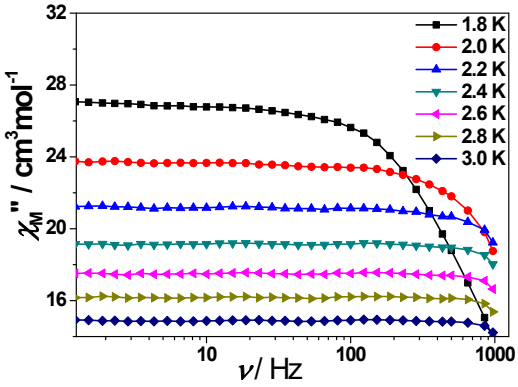

Fig. S7 Frequency-dependent χ_M" AC susceptibilities under zero DC field for **3**.